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(54) Title: RECHARGEABLE LITHIUM ELECTROCHEMICAL CELL			
(57) Abstract			
<p>The invention relates to a rechargeable electrochemical cell comprising a negative electrode, an electrolyte and a positive electrode, characterised in that the positive electrode structure thereof comprises (a) one or more materials selected from the group consisting of LiMn_2O_4, LiCoO_2, LiNiO_2, $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ where $0 < x < 1$, preferably LiMn_2O_4 and (b) one or more materials selected from the group consisting of orthorhombic LiMnO_2, monoclinic LiMnO_2 ($m\text{-LiMnO}_2$), hexagonal LiFeO_2 ($h\text{-LiFeO}_2$), $\alpha\text{-NaMnO}_2$, $\beta\text{-NaMnO}_2$, $\alpha\text{-NaFeO}_2$, and lithium/sodium compounds of the formula $\text{Li}_x\text{Na}_y\text{M(II)O}_{1+1/2(x+y)}$, where $x \geq 0$, $y \geq 0$ and $x+y \leq 2$, and where M(II) is a transition metal in oxidation state +2, selected from the group consisting of Mn, Co, Ni and Fe, preferably $\text{Li}_x\text{Na}_y\text{Mn(II)O}_{1+1/2(x+y)}$, where $x \geq 0$, $y \geq 0$ and $x+y \leq 2$, more preferably $\text{LiNa}_{0.6}\text{MnO}_{1.8}$, the material(s) of group (a) being present in the electrode structure in an amount corresponding to 20-98 % by weight of the complete electrode structure, and the material(s) of group (b) being present in the electrode structure in an amount corresponding to 1-79 % by weight of the complete electrode structure.</p>			

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RECHARGEABLE LITHIUM ELECTROCHEMICAL CELL

This invention relates to rechargeable electrochemical cells of the lithium-ion or lithium-alloy type.

5 The use of non-aqueous electrolytes has allowed the development of high voltage lithium-based electrochemical cells for energy storage. Such cells are further characterised in that their electrodes may be intercalation compounds. The positive electrode structures may be based
10 on transition metal oxides operating at a potential close to 4V vs. Li/Li⁺. Negative electrode structures of carbons and graphites may be applied, which reversibly intercalate lithium at a potential close to the potential of metallic lithium. Such cells are referred to as lithium-ion cells,
15 as the active lithium is always in its ionic form. Alternatively, alloy negative electrode structures like Li-Al and Li-Sn may be used. Such cells will be referred to as lithium-alloy cells. All of the above configurations provide voltages close to 4V.

20 For the cells referred to above one of the limiting factors for their energy density has been a low initial capacity retention. Upon operation, a capacity loss during initial charging of the cells is observed, as is a fading capacity
25 upon extended cycling or storage, which in combination define the initial capacity retention.

The capacity reduction phenomena are ascribed to the instability of the electrolyte towards the electrodes.
30 Instability towards the negative electrode leads to gassing and formation of a passivating film, whereas instability against the positive electrode leads to corrosion of the electrode structure. Both phenomena involve electrolyte decomposition and result in loss of active lithium and a
35 fading capacity of the cell.

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In lithium-ion cells, the losses from the anode reactions dominate the losses at the cathode. The magnitude of the losses merely depends on the type of carbon(s)/graphite(s), the electrolyte and their combination. Using carbon-based anodes, active lithium corresponding to 30-50% of the amount of active lithium in the cell may be lost during the first charge-discharge cycles of the cell, i.e. during the initial charging and the young life of the cell. The use of graphites permits somewhat lower losses in the range 5-30%, however, with poorer long term capacity retention.

In the lithium-ion cell active lithium is provided solely via the cathode. Although prelithiation of carbon/graphite anode structures has been investigated, traditionally lithium-free carbon/graphite structures are applied. Compared to cells based on pure metallic lithium, the loss of active material is rather detrimental. Whereas metallic lithium can be added at 3,800 mAh/g, the specific capacities of the cathode materials are significantly lower.

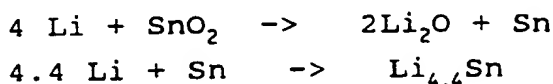
Currently, LiMn_2O_4 is one of the active cathode materials used in lithium-ion cells. The active lithium capacity thereof depends to some extent on the preparation method, but is generally of the order of 122 mAh/g.

Therefore, simply providing additional LiMn_2O_4 to compensate for any loss of active material is somewhat inefficient and may reduce the lithium-ion cell capacity and energy density significantly.

Losses occur in the lithium-alloys cells, too. In the alloy cells with which the present invention is concerned, the

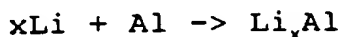
lithium alloys are formed in-situ, as this obviates the need for the difficult handling of low potential lithium compounds, e.g. under inert conditions. In such cells active lithium is provided solely via the cathode.

In one type of alloy cell the base material is provided as an oxide. In the case of tin, the reaction scheme is:



This scheme clearly shows the irreversible loss of lithium in terms of lithium oxide, in this case being in the range of 48% of the total amount of active lithium.

In another type of lithium-alloy cell lithium is simply alloyed into the base metal, such as aluminium or silicon, which is applied directly in the cell. In the case of aluminium, the reaction scheme is:



In such case a loss is observed as the diffusion of lithium in the α -phase of the lithium-aluminium alloy is so slow that lithium therefrom is practically not released during discharge of the cell. Further, the above instability phenomena still exist and cause additional loss of active lithium.

Therefore, there is a need for an efficient concept for providing additional active lithium to compensate for capacity losses in lithium ion cells as well as in lithium-alloy cells. Such active lithium is provided entirely via

the cathode.

A number of patents describes approaches to compensate for the loss of active lithium:

5

US-A-5,429,890 and US-A-5,561,007, both to Valence Technology, suggest the use of LiMO_2 additives ('890: $\text{M}=\text{Ni}, \text{Co}$ and mixtures thereof, '007: $\text{Li}_y\text{-}\alpha\text{-MnO}_2$) to a LiMn_2O_4 based cathode. As the additives mainly display rechargeable capacity, these patents are merely aiming at closing the voltage gap between the 3 V and the 4 V plateaus of the $\text{Li}/\text{LiMn}_2\text{O}_4$ system.

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US-A-5,370,710 to Sony describes a different approach to alleviating the capacity loss, in particular doping of a LiMn_2O_4 cathode material with an additional amount of lithium to obtain a compound $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ compound either by chemical or electrochemical means. A specific chemical doping method is described in US-A-5,266,299 to Bell Communication Research, which involves doping of LiMn_2O_4 or $\lambda\text{-MnO}_2$ with LiI .

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US-A-4,507,371 and US-A-5,240,794, both to Technology Finance Cooperation, describe lithium manganese oxides with excess lithium compared to LiMn_2O_4 . '371 describes cathode structures of $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$, $x>0$, whereas '794 describes a range of compositions within the compositional area defined by the corner compositions $\text{Li}_{14}\text{Mn}_5\text{O}_{12}$, $\text{Li}_2\text{Mn}_3\text{O}_4$, LiMn_3O_4 and $\text{Li}_4\text{Mn}_5\text{O}_{12}$, including $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ where $x\geq 0.25$.

30

Although a number of approaches exists for the introduction of additional active lithium into rechargeable lithium cells, there is still a need for additives to cathodes of

such cells, which provide high capacity, safe and simple processing and which are low cost compounds.

A number of patents describe the use of alkali metal transition metal oxide cathode materials.

US-A-3,970,473 to General Electric Company discloses a solid state electrochemical cell, the cathode comprising a non-stoichiometric lithium compound of the composition $\text{Li}_x\text{Mn}_y\text{O}_z$, $0 < x < 1$ and $0 < y \leq 3$ and z has a value to obtain electrical neutrality. Although such compositions include LiMnO_2 structures, the patents does not suggest the use of such compounds as an additive to LiMn_2O_4 -cathode structures.

US-A-4,302,518 by Goodenough and Mizushima describes an $\text{A}_x\text{M}_y\text{O}_2$ structure (A: Li, Na, K, M: transitions metal, $x < 1$, $y \approx 1$) having the layers of $\alpha\text{-NaCrO}_2$, which is monoclinic. The patent, however, does not disclose on the use of such compounds as an additive to LiMn_2O_4 -cathode structures.

US-A-4,668,595 to Asahi describes a secondary battery with a negative electrode of a carbonaceous material and a positive electrode of layered composite oxide of the formula $\text{A}_x\text{M}_y\text{N}_z\text{O}_2$, where A is an alkali metal, M is a transition metal, N is selected from the group of Al, In, and Sn, and $0.05 \leq x \leq 1.10$, $0.85 \leq y \leq 1.00$ and $0.001 \leq z \leq 0.10$, respectively. The patent, however, does not suggest composite cathode structures.

US-A-5,316,875 to Matsushita discloses a process for the lithiation of LiMn_2O_4 , LiMnO_2 , LiCoO_2 , LiNiO_2 , LiFeO_2 or $\gamma\text{-V}_2\text{O}_5$ by exposure to butyllithium, phenyllithium or naphtyllithium. The patent, however, does not suggest use

of the cathode active materials as additives to LiMn_2O_4 -cathode structures.

5 US-A-5,352,548 to Sanyo describes the use of cathode materials selected from V_2O_5 , TiS_2 , MoS_2 , LiCoO_2 , LiMnO_2 , LiNiO_2 , LiCrO_2 , LiMn_2O_4 and LiFeO_2 in a secondary cell with a vinylene carbonate containing electrolyte. The patent does not describe the use of these cathode materials in composite cathode structures.

10 US-A-5,358,805 also to Sanyo describes the use of the materials FeS_2 , MoS_2 , TiS_2 , LiNiO_2 , LiMn_2O_3 , LiFeO_2 , LiCoO_2 and MnO_2 as cathode in a secondary battery with a BC_3N -anode. The concept of composite cathodes is not described in this patent.

20 US-A-5,478,672 to Sharp describes a secondary cell based on a lithium manganese oxide cathode, which is characterised by having an X-ray diffraction pattern ($\text{CuK}\alpha$) which shows at least three peaks in the ranges $15.2\text{--}15.6^\circ$, $18.6\text{--}18.8^\circ$ and $24.5\text{--}25.1^\circ$, the lithium manganese oxide typically having a chemical composition Li_xMnO_y , $0.8 < x < 1.2$ and $1.9 < y < 2.2$. Although the X-ray diffraction patterns of the above lithium manganese oxide and of the lithium manganese oxide used according to the present invention have at least one common peak, the patent does not describe the use of such compounds in a combined cathode application with LiMn_2O_4 .

30 US-A-5,506,078 to National Research Council of Canada describes a method of forming a spinel-related $\lambda\text{-Li}_{2-x}\text{Mn}_2\text{O}_4$ by electrochemical deintercalation of lithium from an orthorhombic LiMnO_2 of space group Pmm and unit cell $a=4.572\text{\AA}$, $b=5.757\text{\AA}$ and $c=2.805\text{\AA}$. Although the unit cell

dimensions of the patent is in fair accordance with those of the orthorhombic LiMnO_2 used according to the present invention, the patent does not disclose composite cathodes of LiMnO_2 and LiMn_2O_4 .

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US-A-5,531,920 to Motorola describes a method for the synthesis of AMnO_2 compounds, A being selected from the group of Li, Na, K and their combinations and M being selected from the group of Ti, V, Mn, Cr, Fe, Ni, Co and their combinations. The patent discloses a method in which $\text{M}(\text{OH})_2$ is reacted with oxidizing compounds selected from the group of Li_2O_2 , LiNO_3 , LiClO_4 , Na_2O , K_2O_2 and their combinations. The patent, however, does not disclose the use of such compounds as an additive to LiMn_2O_4 -cathode structures.

15

US-A-5,558,961 to The Regents of the University of California, describes an orthorhombic alkali metal manganese oxide secondary cell based on a cathode active material $\text{M}_x\text{Z}_y\text{Mn}_{1-y}\text{O}_2$, where M is an alkali metal, Z is a metal capable of substituting for manganese such as iron, cobalt or titanium, $0.2 \leq x \leq 0.75$, and $0 \leq y \leq 0.6$, which is initially formed as $\text{Na}_{0.44}\text{Z}_y\text{Mn}_{1-y}\text{O}_2$. Although the patent discloses orthorhombic LiMnO_2 and its use in electrochemical cells, it does not describe the use of such material as an additive to LiMn_2O_4 -cathode structures. The patent further describes cathodes of lithiated orthorhombic sodium manganese oxide, however, the manganese of the lithium/sodium manganese oxide compounds is in an oxidation state in the range +3 to +4, i.e. higher than the oxidation state of +2 used according to the present invention. Further, the patent does not give any teaching on the use of such material as an additive to LiMn_2O_4 -cathode structures.

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US-A-5,561,006 to SAFT describes a rechargeable cell with a cathode including at least one orthorhombic substance which is a yellow-green single phase oxide of lithium and manganese with lattice parameters $a = 0.459 \pm 0.004 \text{ nm}$,
5 $b = 0.577 \pm 0.004 \text{ nm}$ and $c = 0.281 \pm 0.003 \text{ nm}$ and a molar ratio of Li and Mn in the range 0.85-1.10. Although the lattice parameters of the black orthorhombic LiMnO_2 used according to the present invention are within the range given by SAFT, the patent does not describe the use of the yellow-
10 green oxide as an additive to LiMn_2O_4 -cathode structures.

The present invention provides rechargeable lithium cells wherein the extra cathode material needed to alleviate the consequences of the capacity loss referred to above is one
15 or more components which have higher specific capacities than that of the rechargeable cathode material.

The substituted capacity may be non-rechargeable, since there is no absolute need according to the invention, for
20 the extra cathode material to contribute to the rechargeable capacity of the cathode. The invention is therefore aiming at lithium-ion cells and lithium-alloy cells, which comprise additives, which are able to deliver a substantially higher capacity in the first charge than
25 the rechargeable cathode material itself, but which do not necessarily contribute to the rechargeable capacity upon further cycling of the electrochemical cell. On the other hand, the extra cathode material may contribute to the rechargeable capacity of the cathode and any such
30 additional rechargeable capacity may be beneficial for the performance of the cell.

More specifically the present invention provides electrochemical cells of the lithium-ion and lithium-alloy type, which as additive to their cathode structures comprise one or more compounds selected from a series of alkali metal transition metal oxides which have high first charge capacities.

The present invention provides a rechargeable electrochemical cell comprising a negative electrode, an electrolyte and a positive electrode, characterised in that the positive electrode structure thereof comprises (a) one or more materials selected from the group consisting of LiMn_2O_4 , LiCoO_2 , LiNiO_2 , $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ where $0 < x < 1$, preferably LiMn_2O_4 and (b) one or more materials selected from the group consisting of orthorhombic LiMnO_2 , monoclinic LiMnO_2 (m- LiMnO_2), hexagonal LiFeO_2 (h- LiFeO_2), α - NaMnO_2 , β - NaMnO_2 , α - NaFeO_2 , and lithium/sodium compounds of the formula $\text{Li}_x\text{Na}_y\text{M(II)O}_{1+\frac{1}{2}(x+y)}$, where $x \geq 0$, $y \geq 0$ and $x+y \leq 2$, and where M(II) is a transition metal in oxidation state +2, selected from the group of consisting of Mn, Co, Ni and Fe, preferably $\text{Li}_x\text{Na}_y\text{Mn(II)O}_{1+\frac{1}{2}(x+y)}$, where $x \geq 0$, $y \geq 0$ and $x+y \leq 2$, more preferably $\text{LiNa}_{0.6}\text{MnO}_{1.8}$, the material(s) of group (a) being present in the electrode structure in an amount corresponding to 20-98% by weight of the complete electrode structure, and the material(s) of group (b) being present in the electrode structure in an amount corresponding to 1-79% by weight of complete electrode structure, with the proviso that in the case of the material(s) of group (b) including any of α - NaMnO_2 , β - NaMnO_2 , α - NaFeO_2 and $\text{Li}_x\text{Na}_y\text{M(II)O}_{1+\frac{1}{2}(x+y)}$, the amount of active sodium originally present in the positive electrode should be lower than the amount of lithium originally present in the electrolyte phase, and with the further proviso, that any material of

group (b) in the positive electrode structure should display a higher first charge specific capacity than any material of group (a) in the positive electrode structure.

5 According to the present invention, an electrochemical cell is provided, containing a cathode structure comprising LiMn_2O_4 and a material selected from a series of alkali metal transition metal oxides, a non-aqueous electrolyte comprising one or more lithium salts and an anode which
10 comprises an electrochemically active carbon structure selected from the group of graphite, coke and carbon blacks or an alloy based on a metal, in particular aluminium and silicon, or based on a metal oxide, in particular tin oxides.

15 The alkali metal transition metal oxides used according to the present invention are orthorhombic LiMnO_2 (o- LiMnO_2), monoclinic LiMnO_2 (m- LiMnO_2), hexagonal LiFeO_2 (h- LiFeO_2), α - NaMnO_2 , β - NaMnO_2 , α - NaFeO_2 and mixed lithium/sodium compounds
20 of the formula $\text{Li}_x\text{Na}_y\text{M(II)O}_{1+\frac{1}{2}(x+y)}$, where $x \geq 0$, $y \geq 0$ and $x+y \leq 2$, and where M(II) is a transition metal in its oxidation state +2, selected from the group of Mn, Co, Ni and Fe.

25 Although other transition metal oxides exist, the above compounds are characterised by having high first charge capacities in practical electrochemical cells, i.e. their practical capacities are close to their theoretical capacities. Further, the extraction of lithium proceeds without deterioration of the rechargeable compounds of the
30 cathode, which are stable against the delithiated additive.

In a preferred embodiment of the invention the additive cathode material is monoclinic LiMnO_2 .

In another preferred embodiment of the invention the additive cathode material is orthorhombic LiMnO_2 . Such orthorhombic LiMnO_2 may be characterised by one or more of the following features:

- 5 (1) peaks of full width at half maximum of less than 0.2° at 2θ -values of 25.0° , 39.4° and 45.2° upon XRD analysis using $\text{CuK}\alpha$;
- (2) having been prepared at a temperature higher than 600°C (High Temperature-o- LiMnO_2 , HT-o- LiMnO_2); and
- 10 (3) having a mean particle size in the range $20\text{-}40\mu$. Alternatively, such orthorhombic LiMnO_2 may be characterised by one or more of the following features:
- (4) peaks of full width at half maximum of at least 0.25° at 2θ -values of 25.0° , 39.4° and 45.2° upon XRD analysis using
- 15 $\text{CuK}\alpha$;
- (5) having been prepared at a temperature no higher than 600°C (Low Temperature-o- LiMnO_2 , LT-o- LiMnO_2); and
- (6) having a mean particle size in the range $5\text{-}15\mu$.

20 In another preferred embodiment of the invention the additive cathode material is monoclinic $\alpha\text{-NaFeO}_2$.

In another preferred embodiment of the invention the additive cathode material is selected from the group

25 consisting of lithium/sodium compounds of the formula $\text{Li}_x\text{Na}_y\text{M(II)O}_{1+\frac{1}{2}(x+y)}$, where $x \geq 0$, $y \geq 0$ and $x+y \leq 2$, and where M(II) is a transition metal in oxidation state +2, selected from the group consisting of Mn, Co, Ni and Fe, preferably lithium/sodium compounds of the formula $\text{Li}_x\text{Na}_y\text{Mn(II)O}_{1+\frac{1}{2}(x+y)}$,

30 where $x \geq 0$, $y \geq 0$ and $x+y \leq 2$, more preferably $\text{LiNa}_{0.6}\text{MnO}_{1.8}$.

According to the invention, the lithium containing additives compensate directly for the loss of active lithium in the

cell. Surprisingly, other alkali metal compounds, and in particular those sodium compounds used according to the present invention, may provide compensation as well.

5 In the case of sodium, however, it is additionally required that the amount of sodium in the cathode can be accommodated by the electrolyte. During the first charge of the battery, little or no intercalation of sodium into the anode structure will take place, and during the first discharge
10 of the battery, little or no reintercalation of sodium into the cathode structure should be anticipated. Consequently there should be little or no sodium species in any of the electrodes, so that all or almost all of the sodium should be accommodated in the electrolyte phase. Even in this state,
15 the lithium ion conductivity in the electrolyte phase should be sufficient to allow proper cell operation. Therefore, the original amount of lithium in the electrolyte should be higher than the original amount of sodium in the cathode. In this case the sodium salt of the electrolyte is acting
20 entirely as supporting electrolyte, not taking part in any of the electrode reactions.

The findings of the group of Kanoh (J. Electrochem. Soc. 140 (1993) 3162-66) confirm this observation. This group
25 evaluated the selectivity of LiMn_2O_4 and $\lambda\text{-MnO}_2$ for Li^+ over Na^+ and K^+ . They concluded that especially the lithium-free structure $\lambda\text{-MnO}_2$ showed high selectivity for Li^+ , i.e. that in the presence of Li^+ , no intercalation of Na^+ or K^+ will take place.

30 In a preferred embodiment of the invention the negative electrode consists of a coke or a carbon black. In such an electrochemical cell the cathode composition comprises

rechargeable material and additive in amounts corresponding to 20-98% and 1-79% by weight of the complete electrode structure, respectively, preferably 50-98% and 1-49% by weight of the complete electrode structure, respectively, more preferably 60-94% and 5-39% by weight of the complete electrode structure, respectively, even more preferably 60-80% and 10-30% by weight of the complete electrode structure, respectively, with the proviso that in the case of the group of additives including any of α -NaMnO₂, β -NaMnO₂, α -NaFeO₂ and $\text{Li}_x\text{Na}_y\text{M(II)O}_{1+\frac{1}{2}(x+y)}$, where $x \geq 0$, $y \geq 0$ and $x+y \leq 2$, and where M(II) is a transition metal in oxidation state +2, selected from the group of Mn, Co, Ni and Fe, the amount of active sodium originally present in the positive electrode should be lower than the amount of lithium originally present in the electrolyte phase.

In another preferred embodiment of the invention the negative electrode consists of a graphite. In such an electrochemical cell the cathode composition comprises rechargeable material and additive in amounts corresponding to 20-98% and 1-79% by weight of the complete electrode structure, respectively, preferably 50-98% and 1-49% by weight of the complete electrode structure, respectively, more preferably 80-98% and 1-19% by weight of the complete electrode structure, respectively, even more preferably 80-89% and 1-10% by weight of the complete electrode structure, respectively, with the proviso that in the case of the group of additives including any of α -NaMnO₂, β -NaMnO₂, α -NaFeO₂ and $\text{Li}_x\text{Na}_y\text{M(II)O}_{1+\frac{1}{2}(x+y)}$, where $x \geq 0$, $y \geq 0$ and $x+y \leq 2$, and where M(II) is a transition metal in oxidation state +2, selected from the group of Mn, Co, Ni and Fe, the amount of active sodium originally present in the positive electrode should

be lower than the amount of lithium originally present in the electrolyte phase.

In a preferred embodiment of the invention the electrolyte of the electrochemical cell comprises one or more non-aqueous solvents selected from the group of ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), diethyl carbonate (DEC), γ -valerolactone, γ -butyrolactone and one or more salts selected from the group of LiCF_3SO_3 , LiAsF_6 , LiBF_4 , LiPF_6 and LiClO_4 .

In an alternative embodiment of the invention the rechargeable material is selected from the group of LiCoO_2 , LiNiO_2 , $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ where $0 < x < 1$. These materials have capacities in the range 140-160 mAh/g.

In the following tables and examples $\text{LiNa}_{0.6}\text{MnO}_{1.8}$ is used as a representative of the group of lithium/sodium compounds of the formula $\text{Li}_x\text{Na}_y\text{M(II)O}_{1+\frac{1}{2}(x+y)}$, where $x \geq 0$, $y \geq 0$ and $x+y \leq 2$, and where M(II) is a transition metal in oxidation state +2, selected from the group of Mn, Co, Ni and Fe. The use of $\text{LiNa}_{0.6}\text{MnO}_{1.8}$ as a representative should not be considered as any limitation of the scope of the invention.

Table I below summarises the theoretical and actually measured initial capacities of the additives of the present invention. The specific capacities (mAh/g) are measured in half cells with lithium metal negative electrodes at low rate (C/50). They are determined from the amount of charge passed across the cells in the first charge half cycle and the mass of the active material in the cathodes. The initial capacities are obtained upon first charge to 4.3V, 4.5V and 4.7V vs. Li/Li^+ , respectively.

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Table I. Specific first charge capacities (mAh/g) of oxide cathode additive materials.

5	Oxide Additive	First Charge Capacity (mAh/g)			
		Theoretical	Actual		
			4.3 V	4.5 V	4.7 V
	HT-o-LiMnO ₂	286	155	186	248
	LT-o-LiMnO ₂	286	220	264	-
	m-LiMnO ₂	286	230	243	260
10	h-LiFeO ₂	283	17	40	164
	α-NaMnO ₂	244	112	141	-
	β-NaMnO ₂	244	149	171	-
	α-NaFeO ₂	242	12	120	219
	LiNa _{0.6} MnO _{1.8}	411	293	308	339

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As can be seen from Table I, the first charge capacities of the cathode additives used according to the present invention are significantly higher than the capacity of LiMn₂O₄.

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According to the invention, the first charge capacities of any of the cathode additives should be higher than the first charge capacities (equal to the rechargeable capacities) of any of the rechargeable cathode materials, with which the additives are used in composite cathodes.

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Table II below summarises actually measured rechargeable (reversible) capacities of the additives used according to

the present invention. The specific capacities (mAh/g) are measured in half cells with lithium metal negative electrodes at low rate (C/50). They are determined from the amount of charge passed across the cells in the first discharge half cycle and the mass of the active material in the cathodes. The reversible capacities were measured upon cycling in the potential range 3.5-4.3 V vs. Li/Li⁺.

Table II. Specific reversible capacities (mAh/g) of oxide cathode additive materials.

Oxide Additive	Reversible Capacity (mAh/g)
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HT-o-LiMnO ₂	42
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LT-o-LiMnO ₂	58
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m-LiMnO ₂	72
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h-LiFeO ₂	7
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α-NaMnO ₂	10
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β-NaMnO ₂	12
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α-NaFeO ₂	2
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LiNa _{0.6} MnO _{1.8}	13
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As can be seen from Table II, the cathode additives of the present invention display small but significant rechargeable capacities.

Table III below summarises the initial (first charge) capacities of composite cathode structures comprising mixtures corresponding to 1:1 combinations (by charge) of the indicated cathode additive and LiMn_2O_4 .

The 1:1 combination by charge used in table III and below in table IV and examples 13-16 illustrate the preferred cathode composition in the case of approximately 50% irreversible loss at the anode. In such a case the reversible and irreversible capacities of the cathode would match the reversible capacity and irreversible loss at the anode. The use of the 1:1 by charge combination should not be considered as any limitation of the scope of the invention.

The capacities were measured in half cells with lithium metal negative electrodes at low rate (C/50). They are determined from the amount of charge passed across the cells in the first half cycle and the total amount of oxide in the cathodes structures, i.e. they are specific initial capacities (mAh/g) for the 1:1 by charge composite of additive and LiMn_2O_4 . The initial capacities are obtained upon first charge to 4.5V and 4.7V (vs. Li/Li^+), respectively.

Table III. Specific first charge capacities (mAh/g) of mixed oxide cathode structures.

Cathode composition	First Charge Capacity (mAh/g)	
	4.5 V	4.7V
m- LiMnO_2 + LiMn_2O_4	155	161
α - NaFeO_2 + LiMn_2O_4	146	155

As can be seen from Table III, the first charge capacities of the composite cathode structures of additives of the present invention and LiMn_2O_4 are significantly higher than the capacity of pure LiMn_2O_4 .

Table IV below summarises actually measured rechargeable (reversible) capacities of composite cathode structures comprising mixtures corresponding to 1:1 combinations (by charge) of the indicated cathode additive and LiMn_2O_4 . The specific capacities (mAh/g) are measured in half cells with lithium metal negative electrodes at low rate (C/50). They are determined from the amount of charge passed across the cells in the first discharge half cycle and the mass of the active material in the cathodes, i.e. they are specific reversible capacities (mAh/g) for the 1:1 by charge composite of additive and LiMn_2O_4 . The reversible capacities were measured upon cycling in the potential range 3.5-4.3 V (vs. Li/Li^+).

Table IV. Specific reversible capacities (mAh/g) of mixed oxide cathode structures.

Oxide Composition (w%)	Reversible specific Capacity (mAh/g)		
	Composite	Weighted	sum of individual components
$m\text{-LiMnO}_2 + \text{LiMn}_2\text{O}_4$	31.9:68.1	97	106
$\alpha\text{-NaFeO}_2 + \text{LiMn}_2\text{O}_4$	35.8:64.2	85	79

As can be seen from Table IV, the reversible capacities of the composite cathode structures are in accordance with the

sum of reversible capacities of the individual components, weighted by their relative abundance.

Description of the drawings:

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Figure 1 shows the voltage-capacity relationship for a Li/m-LiMnO₂ couple during first charge and subsequent discharge-charge cycling.

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Figure 2 shows the voltage-capacity relationship for a Li/HT-o-LiMnO₂ couple during first charge and subsequent discharge-charge cycling.

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Figure 3 is a graph which shows the voltage-capacity relationship for a Li/LT-o-LiMnO₂ couple during first charge and subsequent discharge-charge cycling.

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Figure 4 shows the voltage-capacity relationship for a Li/LiNa_{0.6}MnO_{1.8} couple during first charge and subsequent discharge-charge cycling.

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Figure 5 is a graph which shows the voltage-capacity relationship for a Li/composite m-LiMnO₂ + LiMn₂O₄ cell configuration during first charge and subsequent discharge-charge cycling.

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Figure 6 is a graph which shows the voltage-capacity relationship for a Li/composite α-NaFeO₂ + LiMn₂O₄ cell configuration during first charge and subsequent discharge-charge cycling.

Figure 7 shows capacity as a function of the number of charge/discharge cycles for a C/composite LT-o-LiMnO₂ + LiMn₂O₄ cell configuration.

5 Figure 8 is a graph showing capacity as a function of the number of charge/discharge cycles for a C/composite α -NaFeO₂ + LiMn₂O₄ cell configuration.

The invention is illustrated by the following examples:

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Example 1:

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α -NaMnO₂ was prepared from equimolar (Na/Mn=1) amounts of Na₂CO₃ and Mn₂O₃, which were intimately ground and placed in a Ni crucible. The mixture was heated twice to 720°C in air for 20 h and then quenched to room temperature. Between these two firings the powder was reground in a mortar. The final powder was yellowish brown, and powder XRD showed the correct phase of α -NaMnO₂. Indexing of the XRD pattern showed monoclinic lattice parameters. A chemical analysis showed that the stoichiometry was approximately Na/Mn=1 giving a theoretical capacity of 244 mAh/g.

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Example 2:

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Monoclinic LiMnO₂ (m-LiMnO₂) was obtained by ion exchange from α -NaMnO₂ (from example 1) as follows: 8 g (0.0728 mole) of α -NaMnO₂ were stirred in 150 ml solution of n-hexanol and 50 g LiBr (0.575 mole, 7.9 times excess of Li). The mixture was refluxed for 10 h followed by vacuum filtration and washing with 100 ml ethanol. Finally, the powder was washed in methanol and dried at 150°C under vacuum. The powder XRD of the brown powder confirmed that the correct phase with

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less than 5 % impurities was obtained. The pattern has been indexed with a monoclinic unit cell ($a=5.437(3)$, $b=2.809(3)$, $c=5.393(3)$ Å). The theoretical capacity of this material is 286 mAh/g.

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Example 3:

Orthorhombic LiMnO_2 was prepared by reaction between 1.1 mole LiOH (26.4 g) and 0.5 mole Mn_2O_3 (79 g) under flowing N_2 in a stainless steel tube. The starting materials were ground and pressed into pellets. As a loss of Li_2O was observed during 14-17h of synthesis at 760-800°C, an excess of LiOH was used. No intermediate grinding was used since LiOH melts at 450°C, penetrating the entire reaction batch homogeneously. The final powder was blackish brown with shiny particles and powder XRD confirmed that the compound was purely orthorhombic. Chemical analysis of the material also confirmed that the stoichiometry corresponded to a Li/Mn ratio of approximately 1 and an oxidation state of Mn in the range +3 to +3.1. The mean particle size of the material was 30 μ . Being prepared at high temperature, this material is referred to as high temperature orthorhombic LiMnO_2 (HT-o- LiMnO_2).

A similar orthorhombic material, although with broader XRD lines, is available from SEDEMA, Tertre, Belgium. As this material is prepared at a lower temperature than the above 760-800°C, it is referred to as low temperature orthorhombic LiMnO_2 (LT-o- LiMnO_2). From a structural point of view, the two compounds are nearly identical, having the same crystal structure and composition. The broader XRD lines, however, indicate loss of long range order. The mean particle size of the material was 10 μ . The colour of the LT-o- LiMnO_2 is

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dark brown as opposed to the blackish brown HT-O-LiMnO₂ powder. The theoretical capacity of both compounds is 286 mAh/g.

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Example 4:

Hexagonal LiFeO₂ (h-LiFeO₂) was obtained from α -NaFeO₂ by ion exchange at 300°C. 3 g (0.0271 mole) of α -NaFeO₂ were
10 refluxed in 20 g (0.290 mole) of LiNO₃ for 5.5 h. The final batch was washed in 250-300 ml methanol, and subsequently dried at 100°C in air, and at 130°C under vacuum. Powder XRD showed that the dark reddish powder with small shiny particles had the hexagonal phase. The only detectable
15 impurity was the starting material α -NaFeO₂ (less than 5 %). The diffraction pattern yields lattice parameters of $a=2.959(2)\text{\AA}$ and $c=14.55(5)\text{\AA}$, and $V=110.3\text{\AA}^3$. The theoretical capacity is 283 mAh/g.

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Example 5:

β -NaMnO₂ was synthesized from equimolar amounts (Na/Mn=1) of Na₂CO₃ and MnO₂ by a solid state reaction. The batch was treated twice for 17 h at 900°C. Between firings the batch
25 was reground. In order to avoid oxidation, quenching from 750°C was used. The final product was a brown powder of β -NaMnO₂ with a few % of a second phase ascribed to β -Na_xMnO₂, $x<1$. The chemical analysis of the product confirmed the overall stoichiometry to be close to Na/Mn=1. The
30 theoretical capacity of β -NaMnO₂ is 244 mAh/g.

Example 6:

α -NaFeO₂, which is thermodynamically stable below 760°C, was prepared from NaOH in 25 mol% excess and α -Fe₂O₃. After firing at 650°C for 16 h, the hygroscopic reddish orange powder was washed with ethanol to remove excess NaOH. The phase purity was confirmed by powder XRD and no impurities were detected. The theoretical capacity of α -NaFeO₂ is 242 mAh/g.

Example 7:

Synthesis of LiNa_{0.6}MnO_{1.8} (Li₅Na₃Mn₅O₉) has been reported by E. Seipp, and R. Hoppe in *Z. Anorg and Allg. Chem.*, **538** (1986) 123-130. This group obtained the compound by a solid state reaction between simple oxides (Li₂O, Na₂O, MnO) in a Ni bomb at 700°C for 14 days, using a ratio of Li:Na:Mn= 2:1:2.

In the present work Li₂O, Na₂O and MnO were used as well, however in a molar ratio of 1:0.6:1 for Li:Na:Mn. The procedure was slightly modified compared to that reported by Seipp and Hoppes and the batch of 0.3311g Li₂O, 0.4120 g Na₂O and 1.510 g MnO was mixed in a mortar and wrapped in Ni-foil. The synthesis was carried out in the steel tube under flowing nitrogen at 650°C for 14 h followed by 2 h at 700 °C. The final product was a brownish orange powder. X-ray diffraction of the powdered product showed LiNa_{0.6}MnO_{1.8} to be the major constituent, an unknown compound and MnO being the major impurities. Upon full extraction of lithium and sodium, the theoretical capacity of LiNa_{0.6}MnO_{1.8} is 411 mAh/g.

Example 8:

Electrodes containing 69-79 % by weight of m-LiMnO₂ (made as described in example 2), 4.8-5.2 % Teflon and 16-26 % Shawinigan carbon black, were made by mixing the oxide and carbon in a mortar with acetone. After drying, Teflon powder was added followed by grinding for 5-10 minutes, during which a plastic material formed. Electrodes were made from this material by rolling until the thickness of the film reaches 70-100 μ m.

10-17 mg pellets were punched from the film, and dried under vacuum at 120-130°C for 14h. Such electrodes were cycled in spring loaded lithium metal based test cells, separated from the counter lithium electrode sheet by a porous glass fiber sheet, or alternatively a porous Celgard separator where applicable, soaked in the electrolyte. Two electrolyte configurations were used, EC/PC (1:1 by volume) with 1M LiPF₆ and 1M LiBF₄, respectively.

Cells were tested under galvanostatic charge conditions to fixed voltage limits, optionally followed by a period of potentiostatic charging at the upper voltage in order to bring the electrode in a reproducible state before each discharge. The specific capacity was calculated numerically from the voltage/time relationship and the amount of oxide in the electrode. The voltage was measured with lithium as the reference. On the initial charge to 4.7 V the capacity was 260 mAh/g. Cycling between 3.5 and 4.3V provided 28% of the initial capacity, i. e. 72 mAh/g. No differences were observed for the two electrolyte configurations applied. Figure 1 shows the voltage-capacity relation for a Li/m-LiMnO₂ couple.

Example 9:

A cell was made as described in example 8, and using the HT-o-LiMnO₂ material made as described in example 3. The initial charge capacity is 248 mAh/g when charged to 4.7 V vs. Li/Li⁺. Cycling of HT-o-LiMnO₂ between 3.5 and 4.3V showed a stable capacity of 42 mAh/g. Identical results were obtained using any of the salt/solvent combinations of 1 M LiPF₆ or 1 M LiBF₄ in EC/PC (1:1 volume ratio) or EC/DEC (2:1 volume ratio). Figure 2 shows the voltage-capacity relation for a Li/HT-o-LiMnO₂ couple.

Example 10:

A cell was made as described in example 8, substituting LT-o-LiMnO₂ of example 3 for m-LiMnO₂. The electrolyte configurations of example 9 were used. A capacity of 264 mAh/g was observed upon charging to 4.5V vs. Li/Li⁺, higher than for the above HT-o-LiMnO₂. Figure 3 is a graph which shows the voltage-capacity relation for a Li/LT-o-LiMnO₂ couple.

Example 11:

A cell was made as described in example 8, using the α -NaFeO₂ obtained as described in example 6, and using the same electrolyte configurations as described in example 9. The electrochemical behavior of α -NaFeO₂ shows that the material delivers a first charge capacity of about 219 mAh/g when charged at C/50-rate to 4.7 V vs. Li/Li⁺.

Example 12:

A cell was made as described in example 8, using the $\text{LiNa}_{0.6}\text{MnO}_{1.8}$ as obtained in example 7, and the 1M LiPF_6 in EC/DMC (1:1 volume ratio) electrolyte configuration. On the initial charge to 4.7 V the capacity was 339 mAh/g. Cycling between 3.5 and 4.3V provided 4% of the initial capacity, i. e. 13 mAh/g. Figure 4 shows the voltage-capacity relationship for a Li/ $\text{LiNa}_{0.6}\text{MnO}_{1.8}$ couple.

Example 13:

Composite m- LiMnO_2 / LiMn_2O_4 -cathodes were made according to the ratio between the capacities, in such a way that the first charge capacities of the two materials were equal:

Cathode Components	First charge capacity (mAh/g)	Relative content (%)
m- LiMnO_2	260	31.9
LiMn_2O_4	122	68.1

Electrodes and cells were made as described in example 8, using the same electrolytes and lithium as the counter electrode. The m- LiMnO_2 compound is identical to the material described in example 2. The capacities obtained from the first charge (162 mAh/g) corresponded to the weighted first charge capacities of the two materials (166 mAh/g). In subsequent cycles, the capacity (98 mAh/g) was slightly higher than that of the pure LiMn_2O_4 content of the electrode (83mAh/g). In fact, the reversible capacity of the composite was in accordance with the weighted reversible

capacity of the components (106 mAh/g). Figure 5 is a graph which shows the voltage-capacity relationship for a Li/composite $m\text{-LiMnO}_2 + \text{LiMn}_2\text{O}_4$ cell configuration.

5 Example 14:

Composite $\alpha\text{-NaFeO}_2 + \text{LiMn}_2\text{O}_4$ cathodes were made according to the ratio between the capacities, in such a way that the first charge capacities of the two materials were equal:

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	Cathode Components	First charge capacity (mAh/g)	Relative content (%)
15	$\alpha\text{-NaFeO}_2$	219	35.8
	LiMn_2O_4	122	64.2

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Electrodes and cells were made as described in example 8, using the same electrolyte configurations and lithium as counter electrode. The $\alpha\text{-NaFeO}_2$ compound is identical to the material described in examples 6 and 11. The initial capacity of the cell when charged to 4.7V vs. Li/Li^+ was 155 mAh/g, in accordance with the weighted capacity of 157 mAh/g. The capacity in subsequent cycles (86 mAh/g) was slightly higher than the weighted value of 79 mAh/g. Figure 6 is a graph which shows the voltage-capacity relationship for the Li/composite $\alpha\text{-NaFeO}_2 + \text{LiMn}_2\text{O}_4$ cell configuration.

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Example 15:

Composite $\text{LT-o-LiMnO}_2/\text{LiMn}_2\text{O}_4$ electrodes were made by mixing 85 % by weight of mixed oxide (1:1 charge ratio), 10 % by

weight of Shawinigan Black and 5 % by weight of polymer binder. The mixture was treated in a ball mill for 17 hours until a uniform ink was formed. Electrodes were made by screen printing onto aluminum current collectors. Subsequently, excess solvent was evaporated and the electrodes were dried at about 50°C for 16h.

A carbon anode was prepared in a similar manner by milling a mixture of 86% by weight of Conoco LSR as active carbon, 10% by weight of Shawinigan Black as conductive carbon diluent and 4% by weight of EPDM as binder. The anode ink was screen printed onto copper foil current collectors.

Cells were assembled as described in example 8 substituting the carbon anode foil for lithium foil. The same electrolyte configurations were employed.

The cell composition was based on the assumption that the anode irreversible loss is approx. 50%. The above cathode is composed accordingly, i.e. half of the cathode initial capacity originating from the "reversible" LiMn_2O_4 and half of the capacity originating from the "irreversible" LT-o-LiMnO_2 . Further, the ratio between the anode and cathode capacities, reversible as well as irreversible, were adjusted in such a way that the anode capacity was approximately 10 % higher than the cathode capacity. This construction was made to eliminate the risk of plating of metallic lithium on the carbon anode, and ensured that all LT-o-LiMnO_2 would be needed in order to compensate the capacity loss of the anode.

During the first high rate charge of the cell to 5V, a specific capacity of 175 mAh/g was extracted from the

composite cathode, compared to 167 mAh/g for the individual components. During subsequent cycling, a constant capacity of approximately 85 mAh/g was retained, corresponding to the contribution from LiMn_2O_4 (83 mAh/g), i.e. in this case only rather little reversible capacity was observed from LT-o- LiMnO_2 . Figure 7 shows the capacity as function of the number of charge/discharge cycles for a C/composite LT-o- $\text{LiMnO}_2 + \text{LiMn}_2\text{O}_4$ cell configuration.

Example 16:

Composite $\alpha\text{-NaFeO}_2/\text{LiMn}_2\text{O}_4$ electrodes were made as described in example 14 using the same compounds and with a charge ratio of 1:1 between the two cathode active components. A carbon anode was made in the way described in example 15. Cells were assembled as described in example 8 by replacing the lithium foil with the carbon anode foil. A 1 M LiBF_4 in EC/PC (1:1 volume ratio) electrolyte was employed. The capacity extracted during the first charge at low rate to 4.7 V was 155 mAh/g, in accordance with the capacity obtained in lithium metal cells (example 14). In subsequent cycles a capacity corresponding to the rechargeable LiMn_2O_4 capacity was obtained (86 mAh/g). This result is in accordance with the result of example 14, displaying the low rechargeable capacity of $\alpha\text{-NaFeO}_2$. Figure 8 is a graph showing the capacity as function of the number of charge/discharge cycles for a C/composite $\alpha\text{-NaFeO}_2 + \text{LiMn}_2\text{O}_4$ cell configuration.

Claims:

1. A rechargeable electrochemical cell comprising a negative electrode, an electrolyte and a positive electrode, characterised in that the positive electrode structure thereof comprises (a) one or more materials selected from the group consisting of LiMn_2O_4 , LiCoO_2 , LiNiO_2 , $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ where $0 < x < 1$, preferably LiMn_2O_4 and (b) one or more materials selected from the group consisting of orthorhombic LiMnO_2 , monoclinic LiMnO_2 (m- LiMnO_2), hexagonal LiFeO_2 (h- LiFeO_2), α - NaMnO_2 , β - NaMnO_2 , α - NaFeO_2 , and lithium/sodium compounds of the formula $\text{Li}_x\text{Na}_y\text{M(II)O}_{1+\frac{1}{2}(x+y)}$, where $x \geq 0$, $y \geq 0$ and $x+y \leq 2$, and where M(II) is a transition metal in oxidation state +2, selected from the group consisting of Mn, Co, Ni and Fe, preferably $\text{Li}_x\text{Na}_y\text{Mn(II)O}_{1+\frac{1}{2}(x+y)}$, where $x \geq 0$, $y \geq 0$ and $x+y \leq 2$, more preferably $\text{LiNa}_{0.6}\text{MnO}_{1.8}$, the material(s) of group (a) being present in the electrode structure in an amount corresponding to 20-98% by weight of the complete electrode structure, and the material(s) of group (b) being present in the electrode structure in an amount corresponding to 1-79% by weight of complete electrode structure, with the proviso that in the case of the material(s) of group (b) including any of α - NaMnO_2 , β - NaMnO_2 , α - NaFeO_2 and $\text{Li}_x\text{Na}_y\text{M(II)O}_{1+\frac{1}{2}(x+y)}$, the amount of active sodium originally present in the positive electrode should be lower than the amount of lithium originally present in the electrolyte phase, and with the further proviso, that any material of group (b) in the positive electrode structure should display a higher first charge specific capacity than any material of group (a) in the positive electrode structure.

2. A rechargeable electrochemical cell comprising a negative electrode, an electrolyte and a positive electrode, characterised in that the positive electrode structure thereof comprises (a) one or more materials selected from the group consisting of LiMn_2O_4 , LiCoO_2 , LiNiO_2 , $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ where $0 < x < 1$, preferably LiMn_2O_4 and (b) monoclinic LiMnO_2 (m- LiMnO_2), the material(s) of group (a) being present in the electrode structure in an amount corresponding to 20-98% by weight of complete electrode structure, and the monoclinic LiMnO_2 of group (b) being present in the electrode structure in an amount corresponding to 1-79% by weight of the complete electrode structure, with the proviso that the monoclinic LiMnO_2 in the positive electrode structure should display a higher first charge specific capacity than any material of group (a) in the positive electrode structure.

3. A rechargeable electrochemical cell comprising a negative electrode, an electrolyte and a positive electrode, characterised in that the positive electrode structure thereof comprises (a) one or more materials selected from the group consisting of LiMn_2O_4 , LiCoO_2 , LiNiO_2 , $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ where $0 < x < 1$, preferably LiMn_2O_4 and (b) orthorhombic LiMnO_2 , the material(s) of group (a) being present in the electrode structure in an amount corresponding to 20-98% by weight of the complete electrode structure, and the orthorhombic LiMnO_2 of group (b) being present in the electrode structure in an amount corresponding to 1-79% by weight of complete electrode structure, with the proviso that the orthorhombic LiMnO_2 in the positive electrode structure should display a higher first charge specific capacity

than any material of group (a) in the positive electrode structure.

- 5 4. A rechargeable electrochemical cell according to claim 3, wherein the orthorhombic LiMnO_2 is characterised by peaks of full width at half maximum of less than 0.2° at 2θ -values of 25.0° , 39.4° and 45.2° upon XRD analysis using $\text{CuK}\alpha$.
- 10 5. A rechargeable electrochemical cell according to claim 3 or 4, wherein the orthorhombic LiMnO_2 is characterised by being prepared at a temperature higher than 600°C (High Temperature-o- LiMnO_2 , HT-o- LiMnO_2).
- 15 6. A rechargeable electrochemical cell according to any of claims 3 to 5, wherein the orthorhombic LiMnO_2 is characterised by having a mean particle size in the range $20\text{-}40\mu$.
- 20 7. A rechargeable electrochemical cell according to claim 3, wherein the orthorhombic LiMnO_2 is characterised by peaks of full width at half maximum of at least 0.25° at 2θ -values of 25.0° , 39.4° and 45.2° upon XRD analysis using $\text{CuK}\alpha$.
- 25 8. A rechargeable electrochemical cell according to claim 3 or 7, wherein the orthorhombic LiMnO_2 is characterised by being prepared at a temperature no higher than 600°C (Low Temperature-o- LiMnO_2 , LT-o- LiMnO_2).
- 30 9. A rechargeable electrochemical cell according to any of claims 3, 7 or 8, wherein the orthorhombic LiMnO_2 is

characterised by having a mean particle size in the range 5-15 μ .

- 5 10. A rechargeable electrochemical cell comprising a negative electrode, an electrolyte and a positive electrode, characterised in that the positive electrode structure thereof comprises (a) one or more materials selected from the group consisting of LiMn_2O_4 , LiCoO_2 , LiNiO_2 , $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ where $0 < x < 1$, preferably LiMn_2O_4 and
- 10 (b) $\alpha\text{-NaFeO}_2$, the material(s) of group (a) being present in the electrode structure in an amount corresponding to 20-98% by weight of the complete electrode structure, and the $\alpha\text{-NaFeO}_2$ of group (b) being present in the electrode structure in an amount
- 15 corresponding to 1-79% by weight of the complete electrode structure, with the proviso that the amount of active sodium originally present in the positive electrode should be lower than the amount of lithium originally present in the electrolyte phase, and with
- 20 the further proviso that $\alpha\text{-NaFeO}_2$ should display a higher first charge specific capacity than any material of group (a) in the positive electrode structure.
- 25 11. A rechargeable electrochemical cell comprising a negative electrode, an electrolyte and a positive electrode, characterised in that the positive electrode structure thereof comprises (a) one or more materials selected from the group consisting of LiMn_2O_4 , LiCoO_2 , LiNiO_2 , $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ where $0 < x < 1$, preferably LiMn_2O_4 and
- 30 (b) one or more materials selected from the group consisting of lithium/sodium compounds of the formula $\text{Li}_x\text{Na}_y\text{M(II)O}_{1+\frac{1}{2}(x+y)}$, where $x \geq 0$, $y \geq 0$ and $x+y \leq 2$, and where M(II) is a transition metal in oxidation state +2,

selected from the group consisting of Mn, Co, Ni and Fe, preferably $\text{Li}_x\text{Na}_y\text{Mn(II)O}_{1+\frac{1}{2}(x+y)}$, where $x \geq 0$, $y \geq 0$ and $x+y \leq 2$, more preferably $\text{LiNa}_{0.6}\text{MnO}_{1.8}$, the material(s) of group (a) being present in the electrode structure in an amount corresponding to 20-98% by weight of the complete electrode structure, and the lithium/sodium compounds of the formula $\text{Li}_x\text{Na}_y\text{M(II)O}_{1+\frac{1}{2}(x+y)}$, where $x \geq 0$, $y \geq 0$ and $x+y \leq 2$, and where M(II) is a transition metal in oxidation state +2, selected from the group consisting of Mn, Co, Ni and Fe of group (b) being present in the electrode structure in an amount corresponding to 1-79% by weight of the complete electrode structure, with the proviso that the amount of active sodium originally present in the positive electrode should be lower than the amount of lithium originally present in the electrolyte phase and with the further proviso that any material of group (b) in the positive electrode structure should display a higher first charge specific capacity than any material of group (a) in the positive electrode structure.

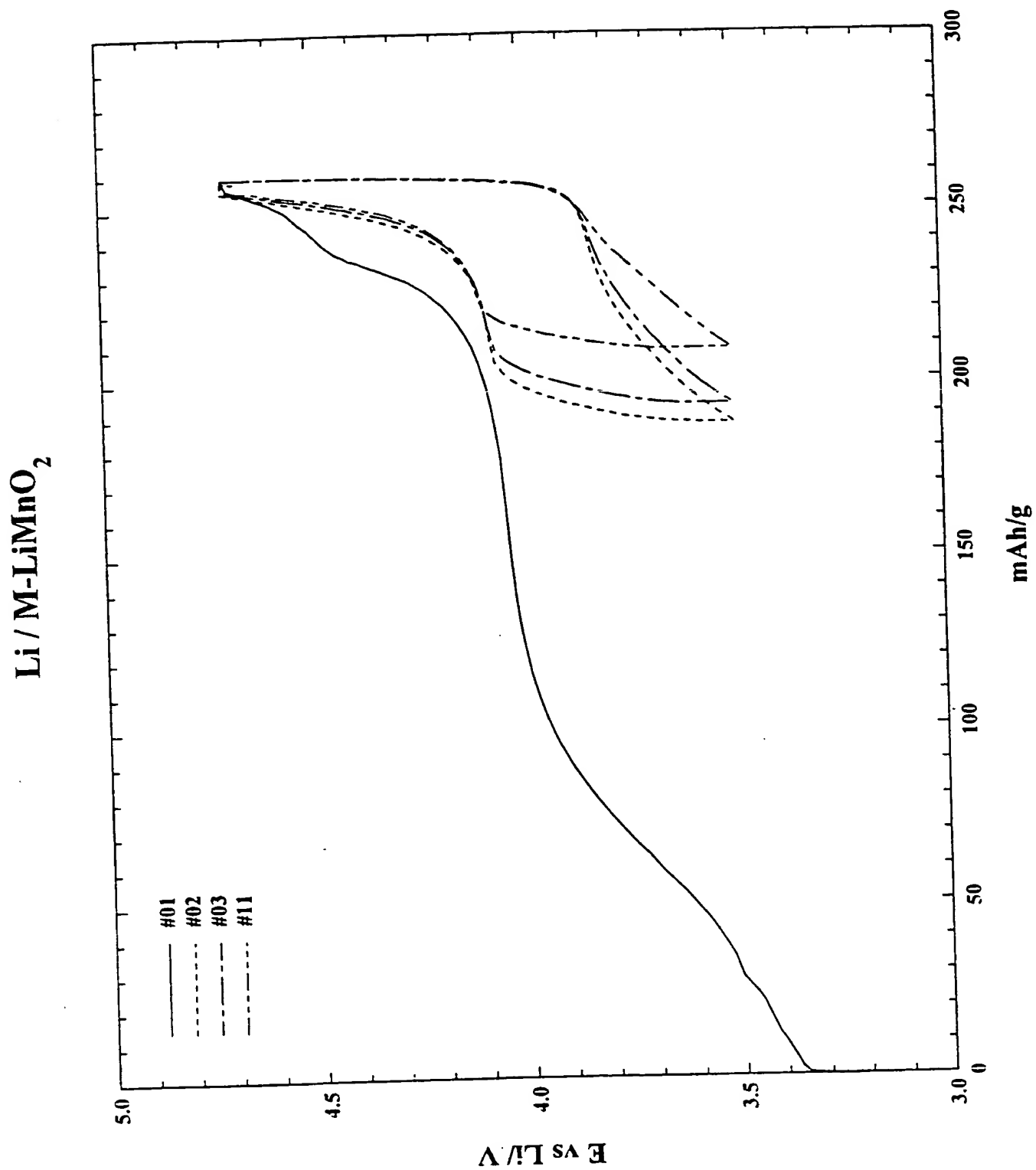
12. An electrochemical cell according to any of claims 1 to 11, in which the negative electrode consists of a metal capable of alloying with lithium, preferably aluminium or silicon, or a metal oxide which can react with lithium to form the corresponding metal capable of alloying with lithium, preferably tin oxide, or a carbon structure capable of intercalating lithium.

13. An electrochemical cell according to claim 12, in which the negative electrode consists of a coke or a carbon black.

14. An electrochemical cell according to claim 13, in which the material(s) selected from the group consisting of LiMn_2O_4 , LiCoO_2 , LiNiO_2 , $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ where $0 < x < 1$ and the material(s) selected from the group consisting of orthorhombic LiMnO_2 , monoclinic LiMnO_2 (m- LiMnO_2), hexagonal LiFeO_2 (h- LiFeO_2), α - NaMnO_2 , β - NaMnO_2 , α - NaFeO_2 and lithium/sodium compounds of the formula $\text{Li}_x\text{Na}_y\text{M(II)O}_{1+\frac{1}{2}(x+y)}$, where $x \geq 0$, $y \geq 0$ and $x+y \leq 2$, and where M(II) is a transition metal in oxidation state +2, selected from the group of Mn, Co, Ni and Fe, preferably $\text{Li}_x\text{Na}_y\text{Mn(II)O}_{1+\frac{1}{2}(x+y)}$, where $x \geq 0$, $y \geq 0$ and $x+y \leq 2$, more preferably $\text{LiNa}_{0.6}\text{MnO}_{1.8}$ is/are present in the electrode structure in an amount corresponding to 50-98% and 1-49% by weight of the complete electrode structure, respectively, preferably 60-94% and 5-39% by weight of the complete electrode structure, respectively, more preferably 60-80% and 10-30% by weight of the complete electrode structure, respectively, with the proviso that in the case of the material(s) of group (b) including any of α - NaMnO_2 , β - NaMnO_2 , α - NaFeO_2 and $\text{Li}_x\text{Na}_y\text{M(II)O}_{1+\frac{1}{2}(x+y)}$, the amount of active sodium originally present in the positive electrode should be lower than the amount of lithium originally present in the electrolyte phase.
15. An electrochemical cell according to claim 12, in which the negative electrode consists of a graphite.
16. An electrochemical cell according to claim 15, in which the material(s) selected from the group consisting of LiMn_2O_4 , LiCoO_2 , LiNiO_2 , $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ where $0 < x < 1$ and the material(s) selected from the group consisting of orthorhombic LiMnO_2 , monoclinic LiMnO_2 (m- LiMnO_2),

hexagonal LiFeO_2 (h-LiFeO_2), $\alpha\text{-NaMnO}_2$, $\beta\text{-NaMnO}_2$, $\alpha\text{-NaFeO}_2$ and lithium/sodium compounds of the formula $\text{Li}_x\text{Na}_y\text{M(II)O}_{1+\frac{1}{2}(x+y)}$, where $x \geq 0$, $y \geq 0$ and $x+y \leq 2$, and where M(II) is a transition metal in oxidation state +2, selected from the group of Mn, Co, Ni and Fe, preferably $\text{Li}_x\text{Na}_y\text{Mn(II)O}_{1+\frac{1}{2}(x+y)}$, where $x \geq 0$, $y \geq 0$ and $x+y \leq 2$, more preferably $\text{LiNa}_{0.6}\text{MnO}_{1.8}$, is/are present in the electrode structure in an amount corresponding to 50-98% and 1-49% by weight of the complete electrode structure, respectively, preferably 80-98% and 1-19% by weight of the complete electrode structure, respectively, more preferably 80-89% and 1-10% by weight of the complete electrode structure, respectively, with the proviso that in the case of the material(s) of group (b) including any of $\alpha\text{-NaMnO}_2$, $\beta\text{-NaMnO}_2$, $\alpha\text{-NaFeO}_2$ and $\text{Li}_x\text{Na}_y\text{M(II)O}_{1+\frac{1}{2}(x+y)}$, the amount of active sodium originally present in the positive electrode should be lower than the amount of lithium originally present in the electrolyte phase.

17. An electrochemical cell according to any of claims 1 to 16, in which the electrolyte comprises one or more non-aqueous solvent selected from the group consisting of ethylene carbonate, propylene carbonate, dimethyl carbonate, diethyl carbonate, γ -valerolactone, γ -butyrolactone and one or more salts selected from the group consisting of LiCF_3SO_3 , LiAsF_6 , LiBF_4 , LiPF_6 and LiClO_4 .



Li / HT-O-LiMnO₂

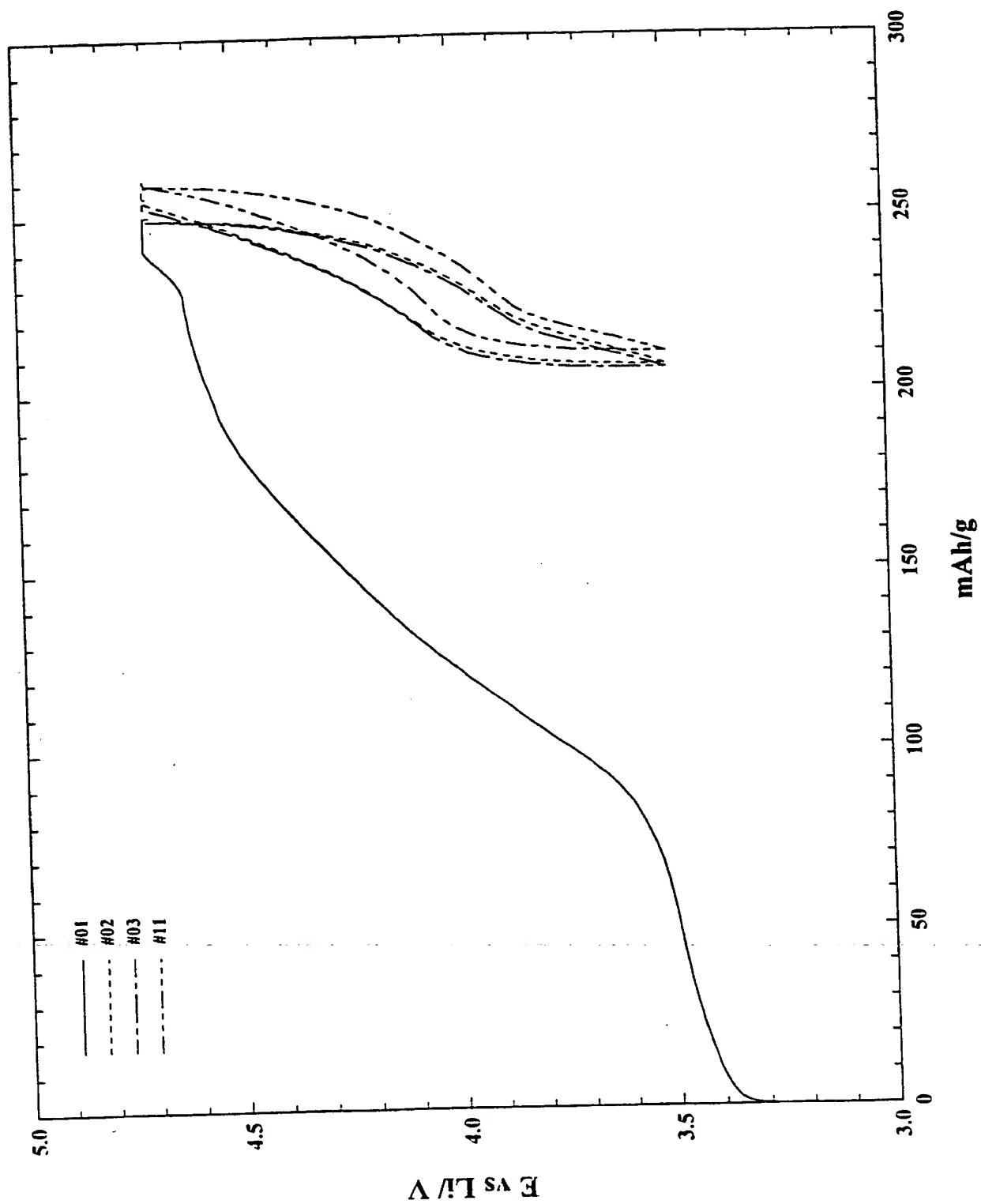


Fig . 2

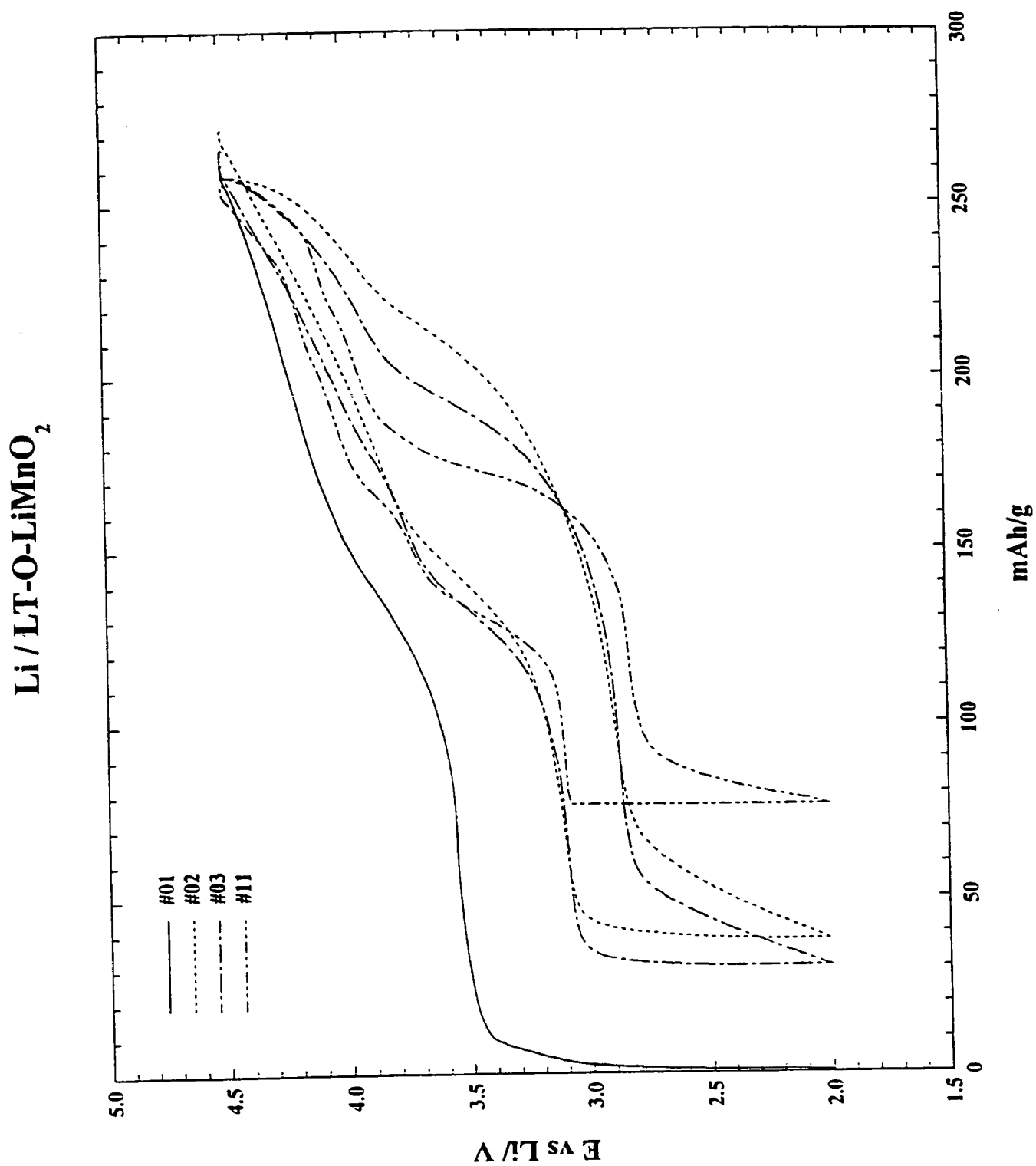


Fig . 3

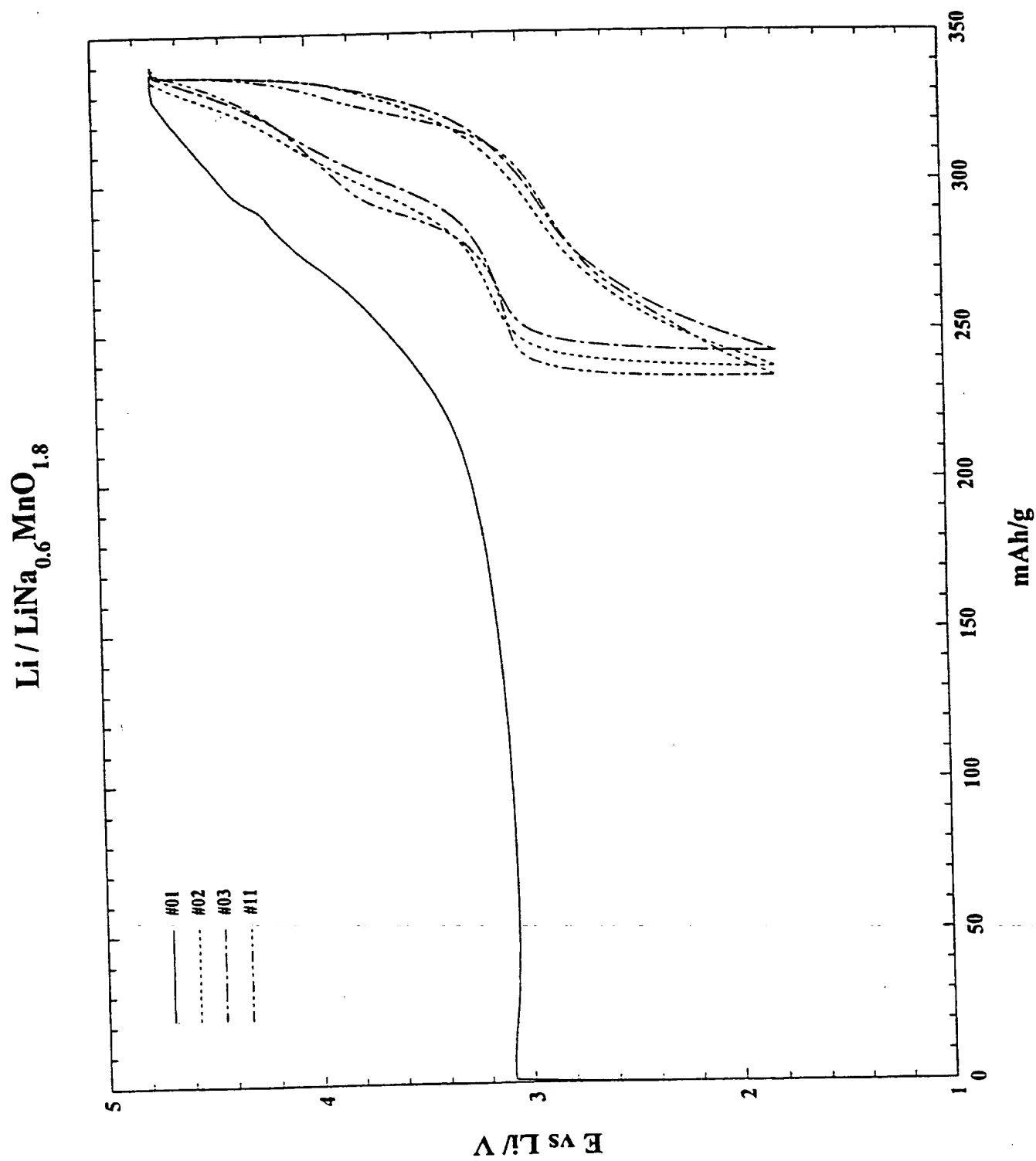


Fig. 4

Li / M-LiMnO₂ + LiMn₂O₄

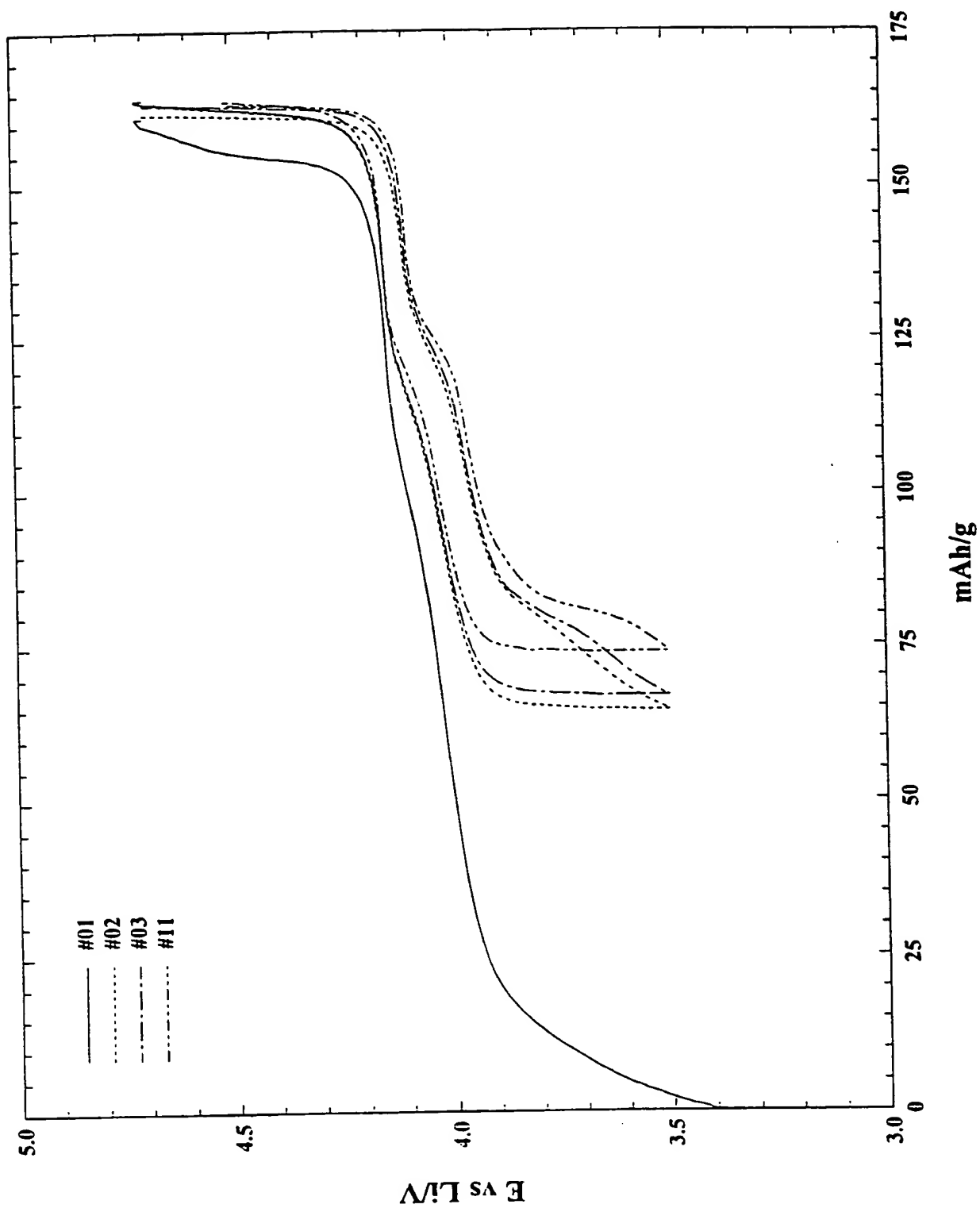


Fig . 5

Li / α -NaFeO₂ + LiMn₂O₄

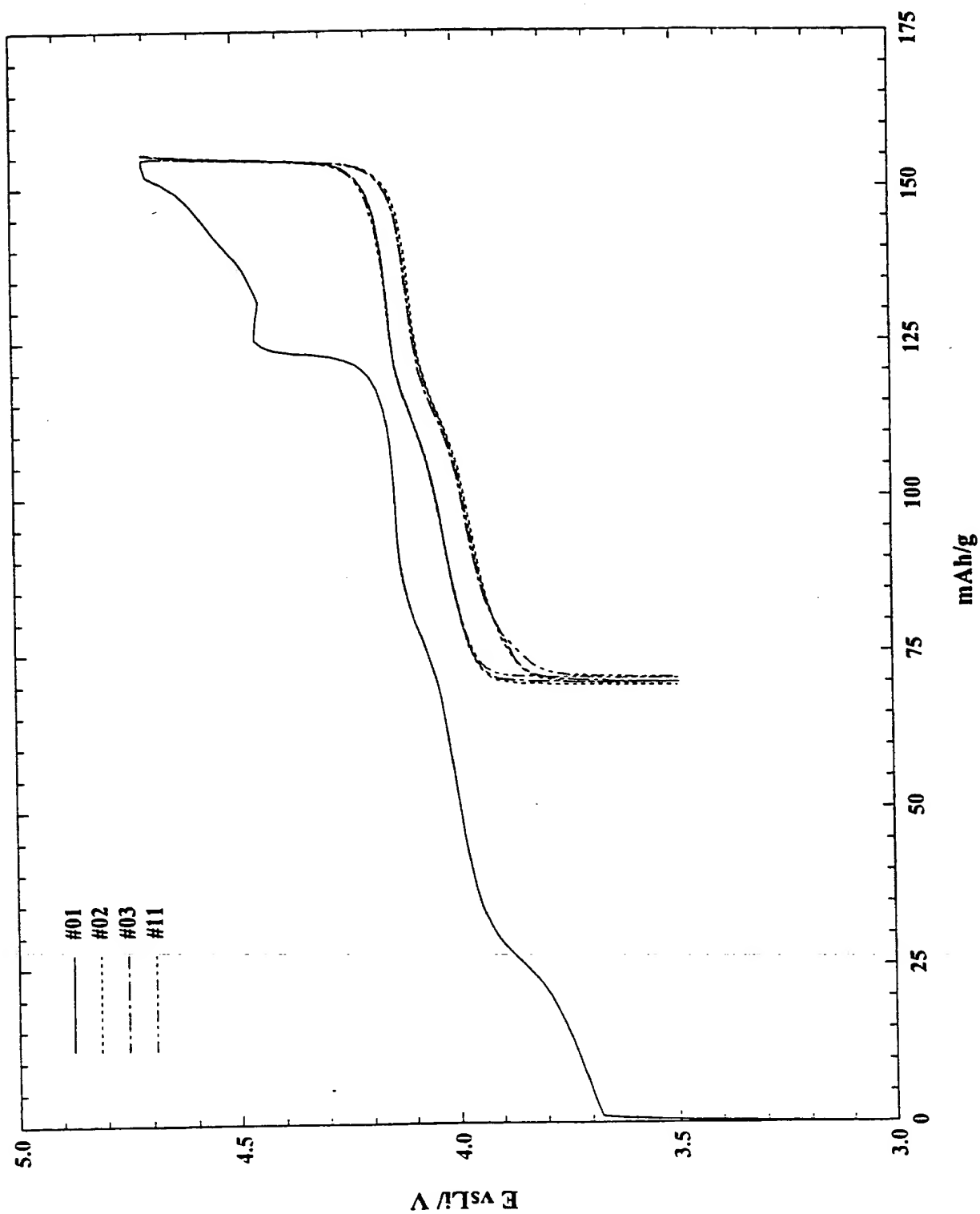


Fig . 6

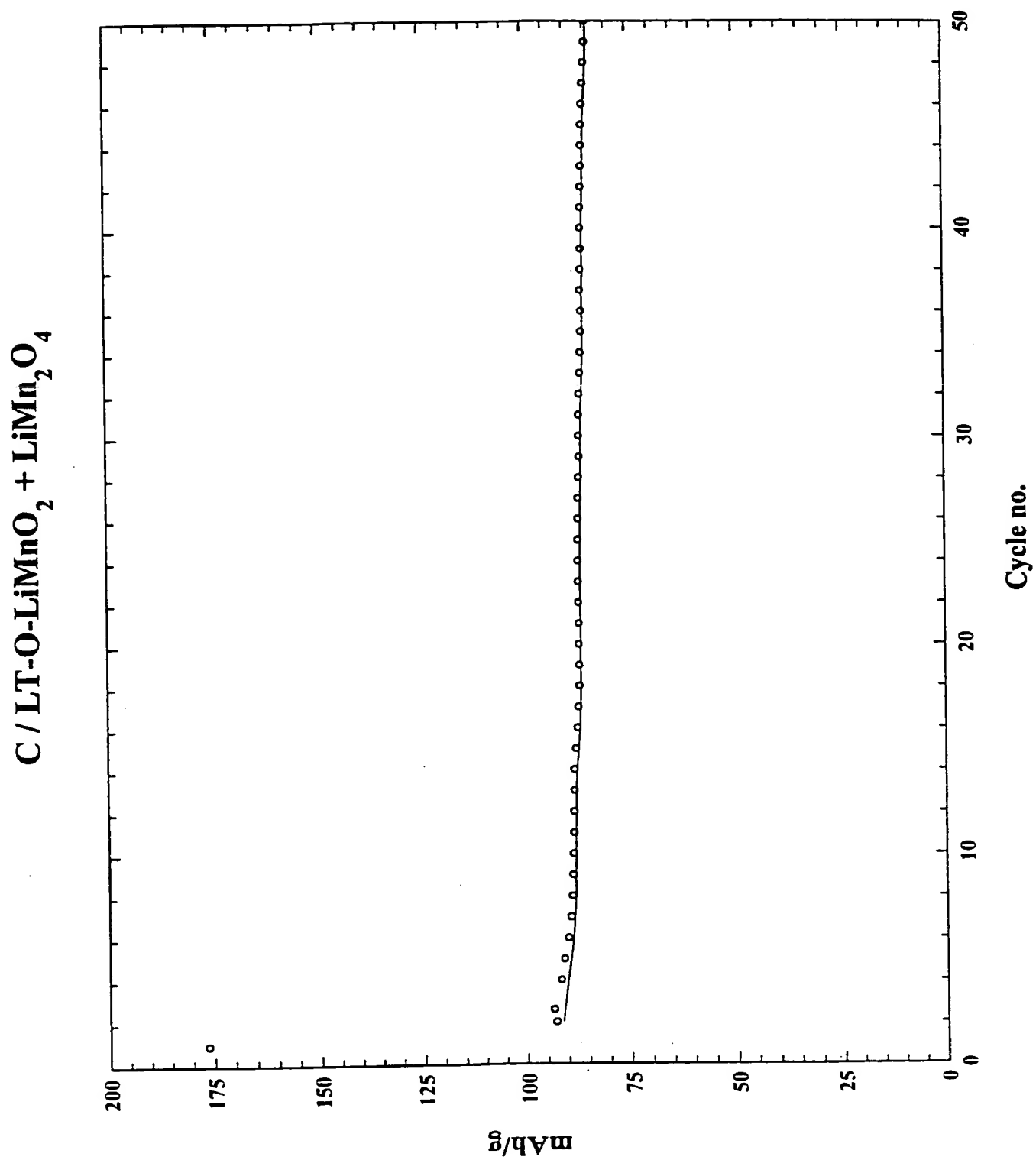


Fig . 7

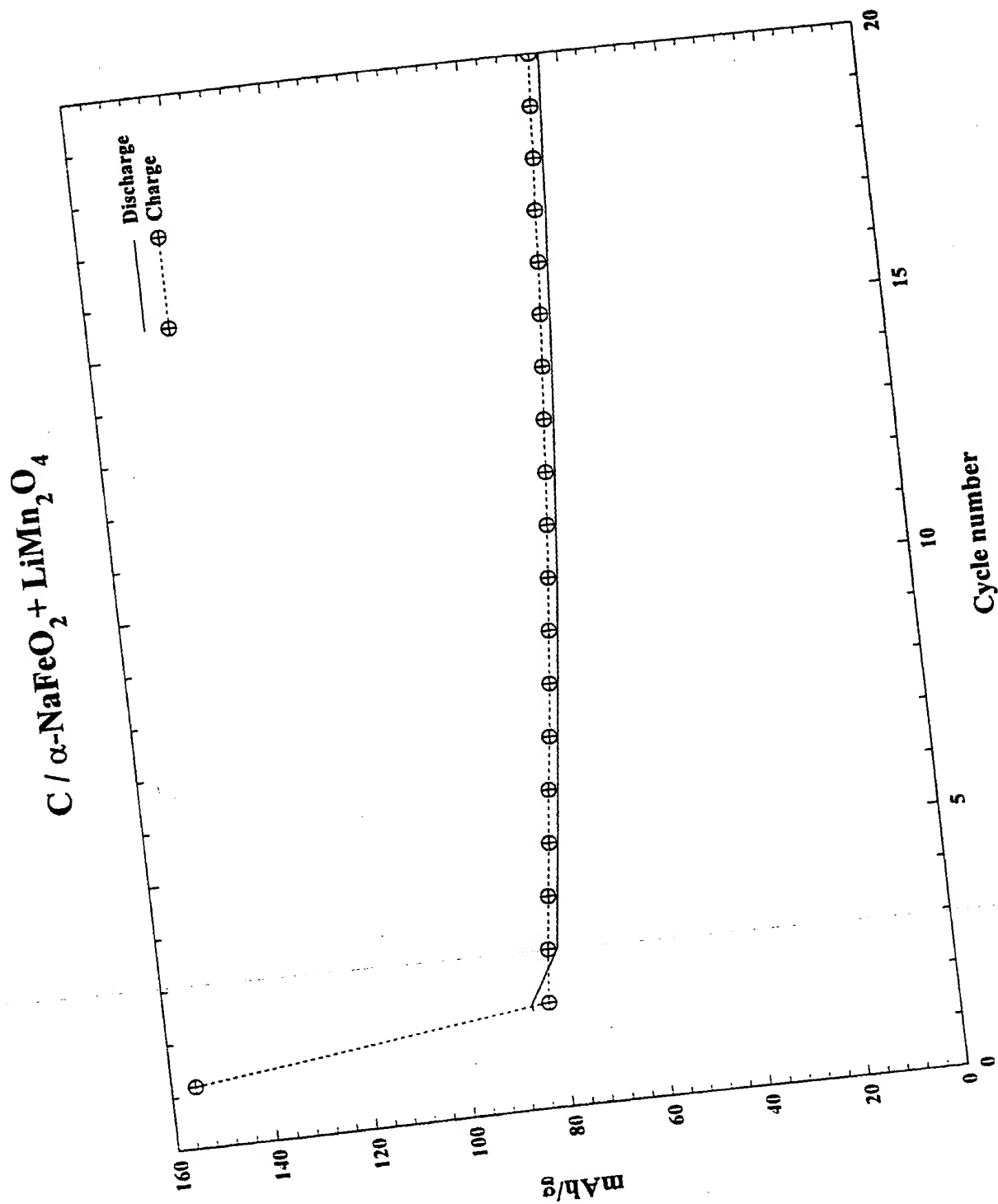


Fig . 8

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 99/02377

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 H01M4/48 H01M4/50

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 096, no. 005, 31 May 1996 (1996-05-31) & JP 08 007883 A (SONY CORP), 12 January 1996 (1996-01-12) abstract	1
A	---	2,3
X	WO 97 01191 A (POLYSTOR CORP) 9 January 1997 (1997-01-09) claim 7; table 2	1,11-17
X	WO 97 48140 A (VALENCE TECHNOLOGY INC ;BARKER JEREMY (US); SAIDI MOHAMED YAZID (U) 18 December 1997 (1997-12-18) page 4, line 17 - page 5, line 16 page 25, line 16 - line 20 --- -/-	1,11-17

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

25 August 1999

Date of mailing of the international search report

03/09/1999

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 99/02377

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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International Application No

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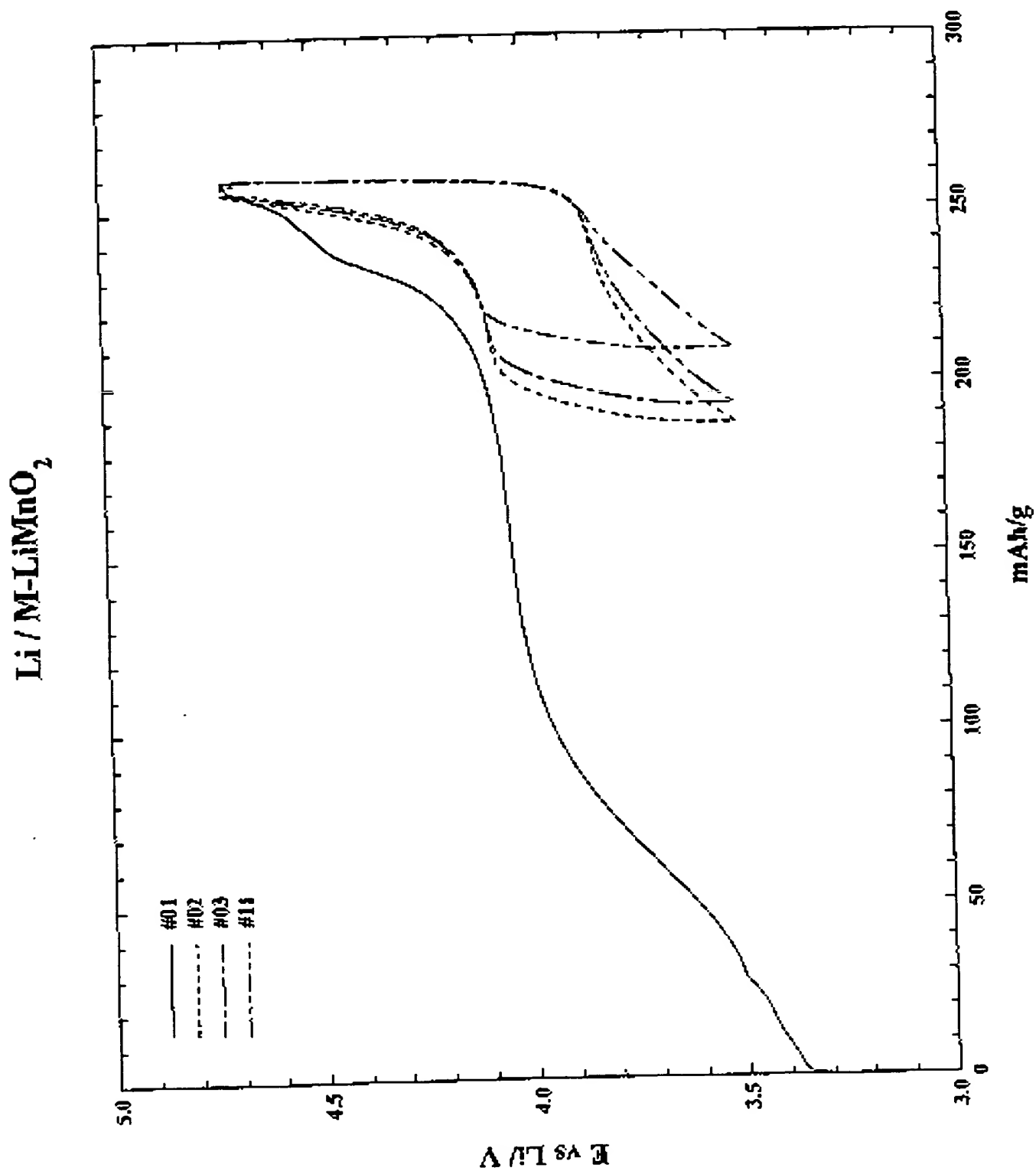
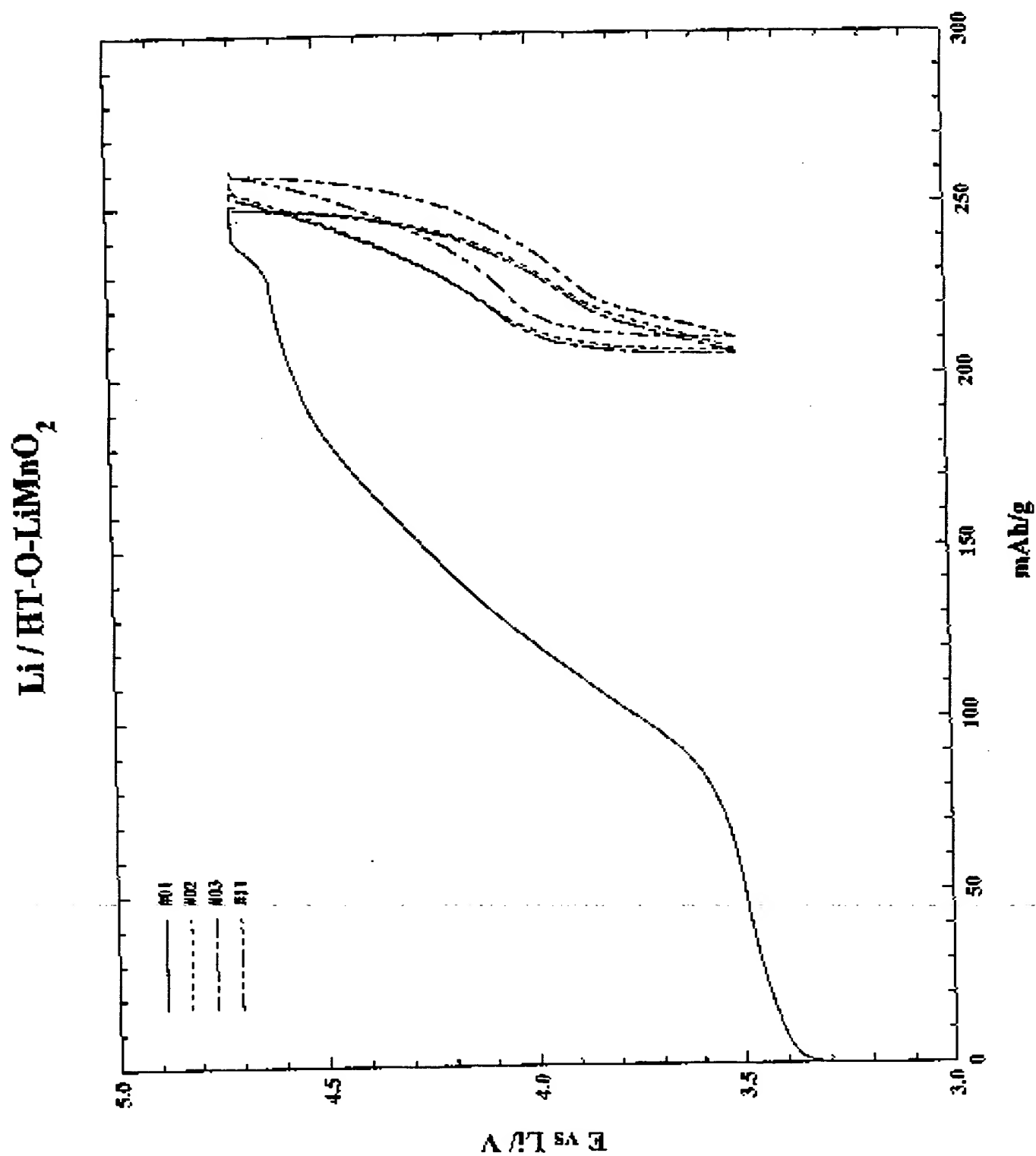
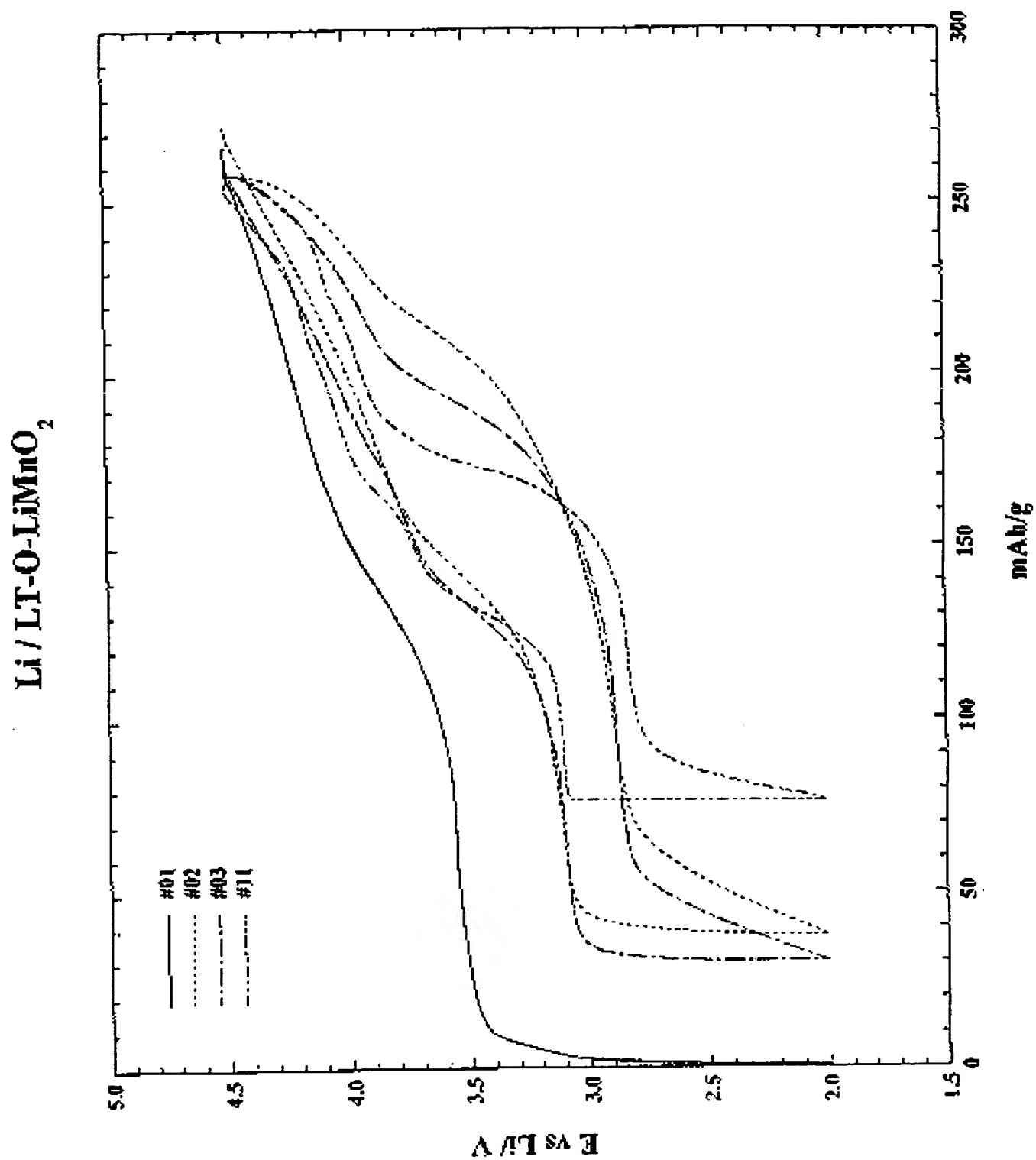


Fig. 1





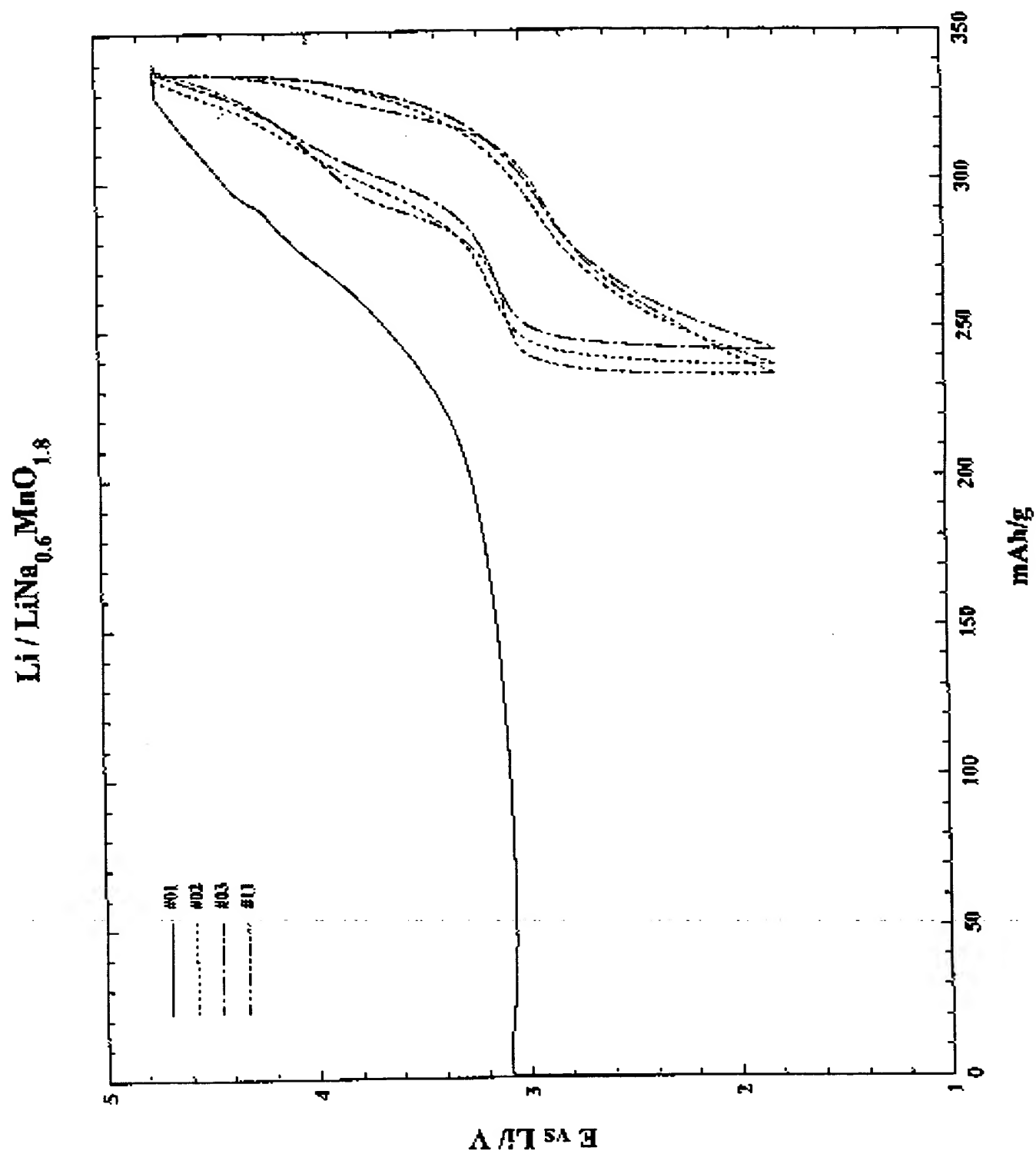


Fig. 4

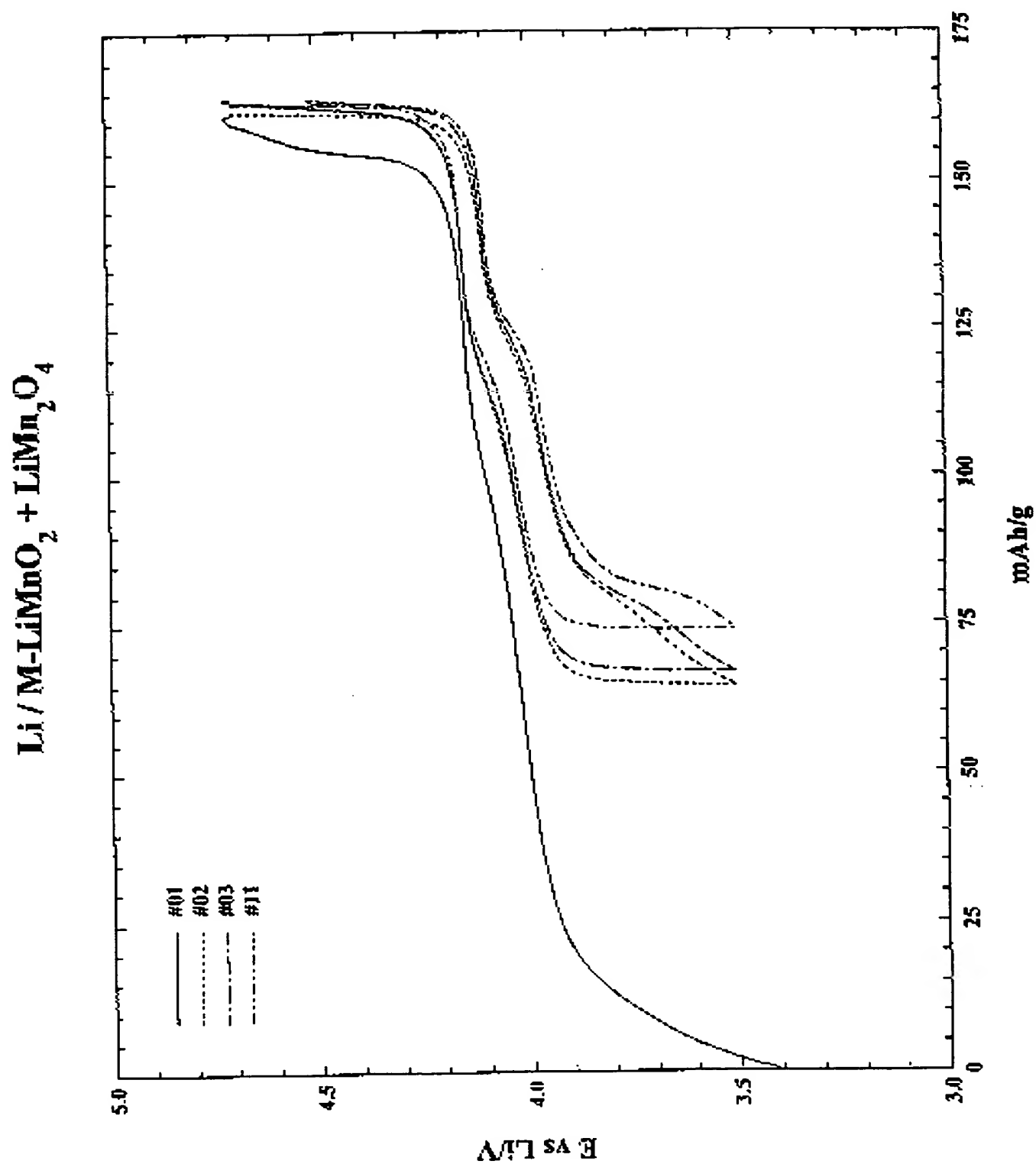


Fig. 5

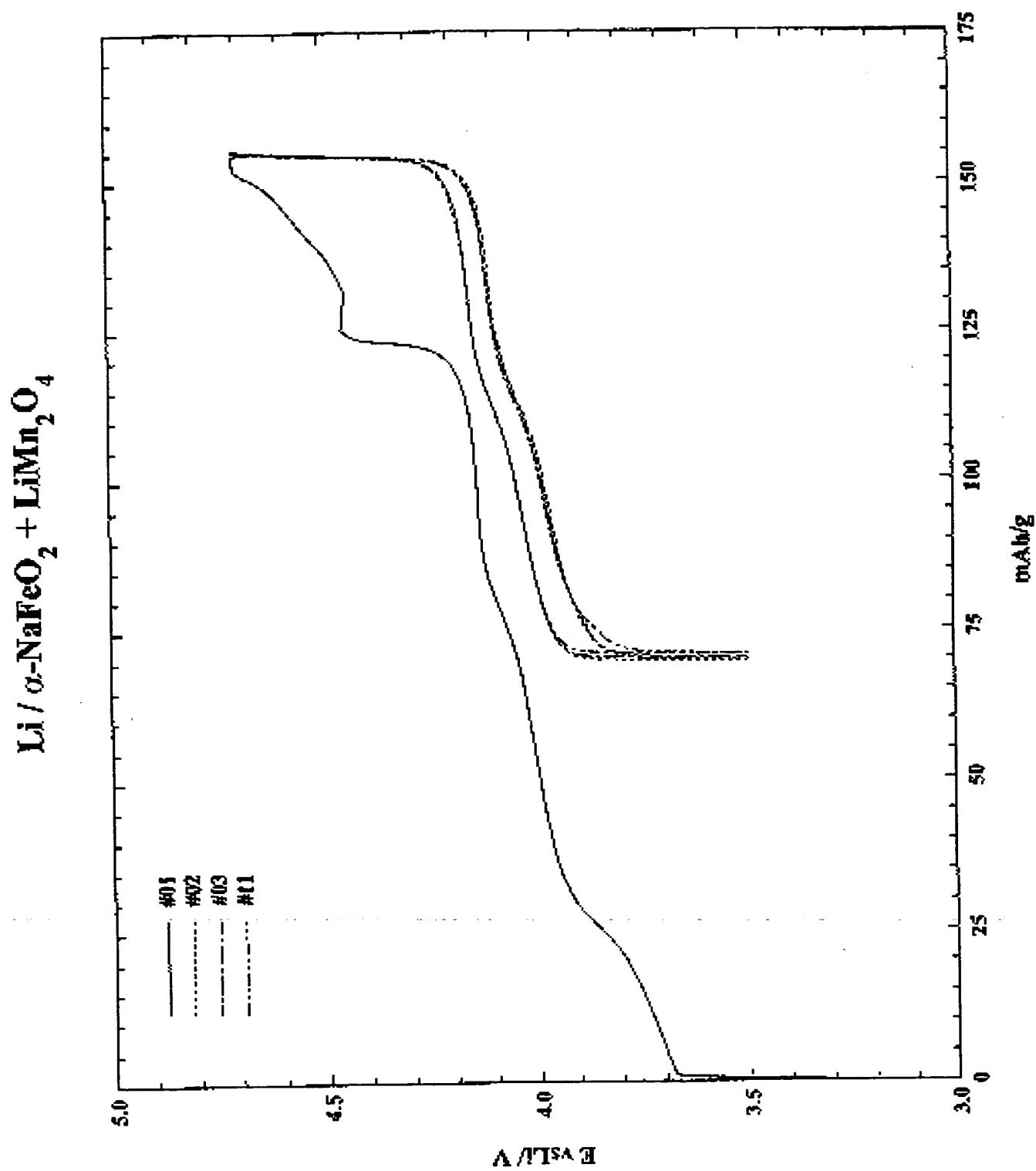


Fig. 6

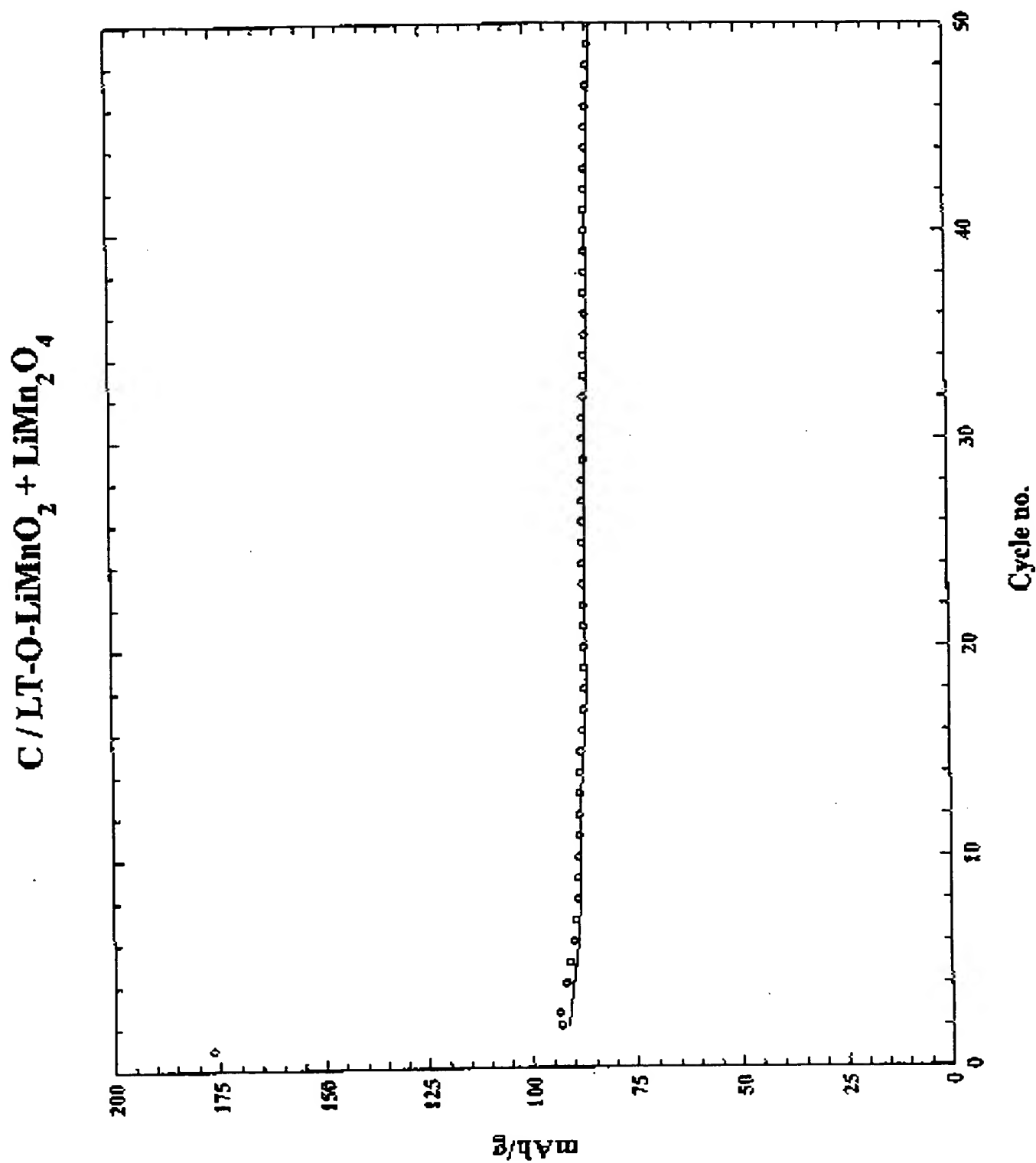


Fig . 7

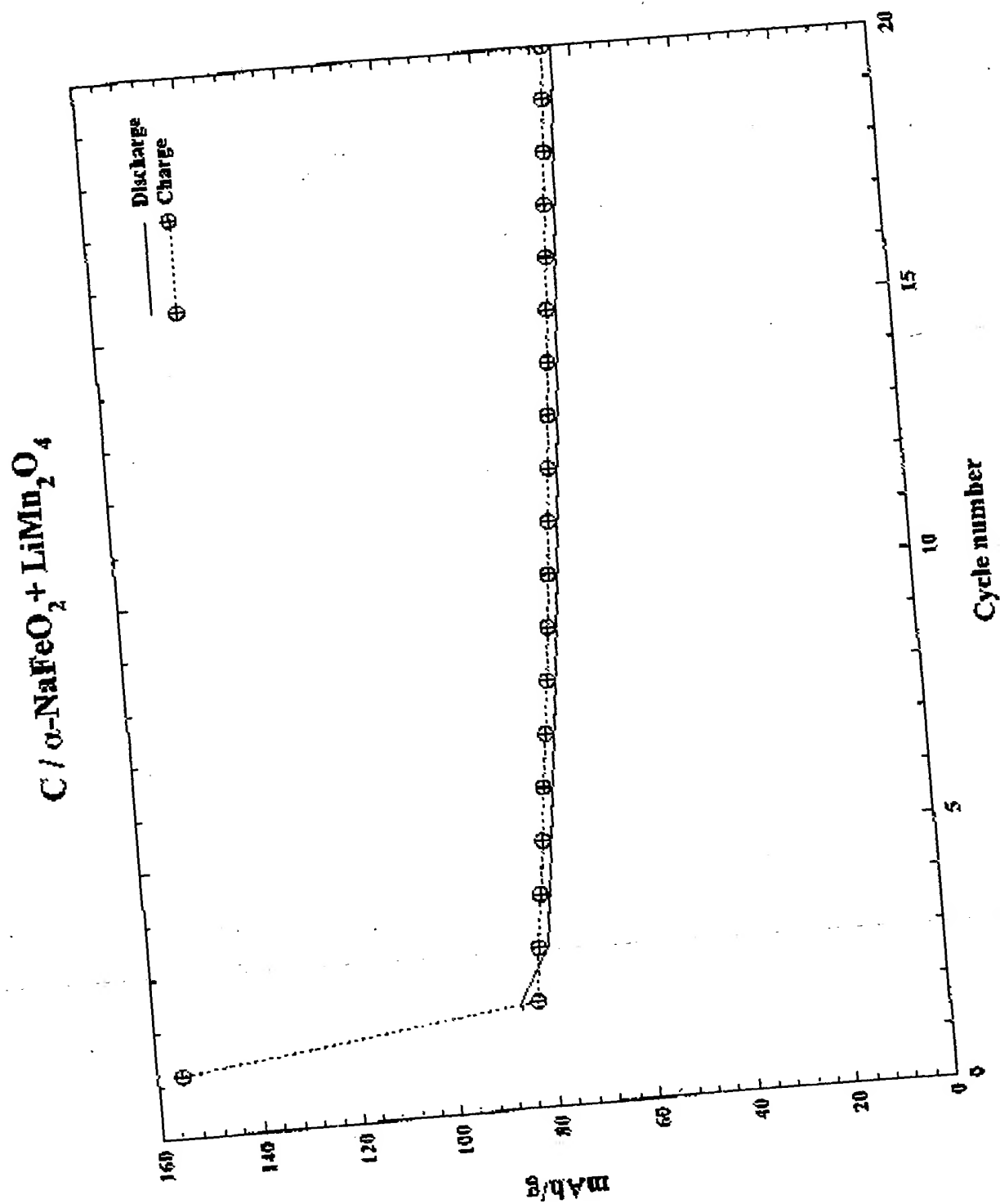


Fig 8